

Synthesis and spectral studies of some metal complexes derived from 1, 3, 4-oxadiazole and evaluated of biological activity

Taleb M. Khrabit and Taghreed M. Musa *

Chemistry department, College of Science, Mustansiriyah University, IRAQ

*Correspondent author email: taghreedmohya@uomustansiriyah.edu.iq

Article Info

Received
29/10/2017

Accepted
13/02/2018

Published
05/05/2019

Abstract

The present work describes the synthesis and characterization of Ligand [L¹] 2, 5-bis(4-butoxy phenyl) -1,3,4- oxadiazole in several steps, one is the treating of 4-hydroxy benzoic acid with alkyl bromide, (RBr) R=[(CH₃(CH₂)₃] in alkaline medium of KOH to give the precursor [S₁] 4-(butyloxy) benzoic acid. The second step have been prepared the precursor [S₂]4-(butyloxy) benzoate from compound [S₁] in methanolic acidic solution. The third step prepared the precursor [S₃] 4-(n-butoxy) benzohydrazide by the reaction [S₂] and hydrazine hydrate(90%). The last step reaction between precursor [S₁] and [S₃] in present of POCl₃ to obtained ligand [L¹]. The primary ligand [L¹] was characterized by Fourier transform infrared spectraFT-IR, ¹H-NMR, ¹³C-NMR, ThermalGravimetric analysis, (UV-Vis) spectrophotometer, Mass spectroscopy and elemental microanalysis (C.H.N) and melting point. The compound benzyl (propane-2-yl) carbamodithioate (S-bpth) was used as co- ligand to synthesis the metal complexes. The Ag(L¹) complex was prepared from two moles of L¹ and one mole of AgNO₃ in dichloromethane solvent at inert condition. The complexes Ni(II), Pd(II), Pt(II), Cu(II) and Zn(II) were synthesized from the two mole of primary ligand(L¹) and one mole secondary ligand (S-bpth) with one m mole of metal chloride in ethanol medium and characterized comprehensively by Fourier transform infrared spectra(FT-IR), (UV-Vis) spectrophotometer, elemental microanalysis (C.H.N) metal analysis, Atomic absorption spectrophotometer (F.A.A), Magnetic moment, Conductivity measurement and some of complexes by Thermal analysis. The results obtained from elemental analyses and spectroscopic measurements have suggested that the Ag(I)-L¹ complex is linear geometry. The mixed ligand complexes of palladium(II), platinum(II) and copper(II) have square planar geometry exceptnickel(II) and Zn(II) complex which is tetrahedral geometry. The second part of the work involved the study of biological activity of the primary 1,3,4-oxadiazole ligand and its metal complexes in DMSO as control against some bacteria strains (*Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia Coli* and *Eterobactern*) with respect to Ampicillin and Ciproflaxine as standard drugs. The observed results from inhibition zone values investigated that most metal complexes exhibited greater inhibition against the all kinds of bacteri zone values that most metal complexes exhibited greater inhibition against the all kinds of bacteria.

Keywords: Cefdinir, Diazotization, Cloud Point Extraction, 2, 5-Dimethylphenol.

الخلاصة

تضمن البحث تحضير وتشخيص الليكند [L¹]=4-(n-butoxy phenyl)-1,3,4-oxadiazole حيث تم تحضير الليكند الأولي [L¹] بارب خطوات تتضمن تحضير المشتق الأول 4-بيوتان حامض بنزويك [S₁] من تفاعل 4-بروموبوتان مع المركب 4-هايدروكسي حامض بنزويك. الخطوة الثانية تتضمن تحضير المشتق الثاني [S₂] من تفاعل المشتق الأول [S₁] مع كحول الميثانول بمحلول حمض من حامض الكبريتيك المركز. الخطوة الثالثة من التفاعل تتضمن تحضير المشتق الثالث [S₃] من خلال تفاعل المشتق الثاني مع الهيدرازين بوجود الإيثانول. الخطوة الرابعة تتضمن تحضير الليكند [L¹] من تفاعل المشتق الأول S₁ مع المشتق الثالث S₃ بوجود POCl₃. تم تشخيص الليكند الأولي [L¹] المحضر بواسطة أطياف الأشعة تحت الحمراء FT-IR وتحليل طيف الرنين النووي المغناطيسي (¹H, ¹³C NMR) وطيف الكتلة (Mass spectra) وطيف الأشعة فوق البنفسجية (UV-Vis) والتحليل الحراري (Analysis Thermal) وتحليل العناصر بواسطة التحليل الدقيق للعناصر (C.H.N). كما تم تحضير الليكند الثانوي [Sodium benzyl (propane-2-yl) carbamodithioate (S-bpth)]، كما تضمن البحث تحضير سلسلة من معقدات أيونات الفلزات لليكند كذلك تم تحضير

معقد الفضة باضافه مولين من الليكند $[L^1]$ مع مول واحد من نترات الفضة بوجود CH_2Cl_2 كمذيب. كما تم تحضير سلسله من معقدات النيكل، البلاديوم، البلاتين، النحاس، والخاصين وذلك من مزج مولين من $[L^1]$ كليكند أولي مع مول واحد من الليكند الثانوي $[S-bpht]$ مع أيونات الفلزات المذكورة أعلاه. تمت دراسة وتشخيص المعقدات الفلزية المحضرة بعد تنقيتها وعزلها بالحالة الصلبة، بتقنيه الأشعة فوق البنفسجية VU-Visb والأشعة تحت الحمراء FT-IR وقياس التوصيلية المولارية وقياس درجة الانصهار والحساسية المغناطيسية وتعيين محتوى الفلز باستخدام تقنية الامتصاص الذري لجميع المعقدات المزج ليكند. وبناءً على النتائج، أثبتت الدراسة أن لمعقد الفضة شكل خطي. ولمعقدات المزج اقترحت الأشكال الفراغية حيث اتخذت معقدات النيكل والخاصين الشكل رباعي السطوح بينما اتخذت معقدات البلاديوم، البلاتين، النحاس شكل مربع مستوي. أما الجزء الثاني من البحث التطبيقي من البحث تضمن دراسة الفعالية البايولوجية لبعض المعقدات المذكوره و ضد بعض أنواع من البكتريا شملت الأنواع التالية: *Staphylococcus aureus*, *Bacillus subtilis*, *Escherichia Coli*, *Eterobactern* وتمت مقارنتها مع الدوائين ciprofloxine و ampicillin. وقد أظهرت النتائج أن جميع المعقدات تمتلك فعالية بايولوجية وينسب متفاوتة.

1. Introduction

The preparation of hetero cyclic compounds and derivatives have very important in later years as these can be found in a large number of compounds which offer biological activities[1]. Heterocyclic derivatives containing nitrogen, sulfur and oxygen that form a large of natural product important applications in different field and biologically[2]. Heterocyclic compounds particularly five and six member heterocyclic have attracted the attention of pharmaceutical community over the years due to their therapeutic values[3]. Among their different derivatives pyroazole and zanies appears aboard spectrum of application in medicinally chemistry and industry They are included in large bio chemical materials like nucleic acid which contain of long chains of hetero cyclic units (nucleotides)[4]. Therefore, researchers have been interested in the development of versatile methods for prepared of these ligands and complexes. The derivatives have established much consideration on relation of their important pharmacological effects, such as anti-cancer[5], anti-viral[6], antimicrobial[7], analgesic, anti-depressant, antifungal effects activities, anti-HI, anti-tumor herbicidal, anti-depressive, anti-Parkinson and anti-convulsion activities[8]. Dithiocarbamate (DTC) formed an important part of biologically active ligands[9]. An extremely large number of dithiocarbamate complexes with transition and non-transition metal ions have been known. The chelating property of DTC arises from the π -electron flow from the nitrogen atom to the sulphur atom via a plane delocalized π -orbital system. The net effect of such an electron flow is strong donation to metal, resulting in a high electron

density on the metal[10][11]. The development of researches in this field encouraged us in this recent paper to give objectivity to give the route of mixed ligands of $[L^1]$ as primary ligand and $[L^2]$ of thiocarbamate salt as secondary ligand to get the solid phase of complexes with high quality.

2. Experimental

2.1. Instrumentation

All the chemicals and starting material used were analytical annular and of highest purity. The intermediates using to prepare Ligand were done on GC MS -QP 2010 VLTRA at department of chemistry, College of science, Mustansiriyah University. The thermal analysis TG and DSC (Differential Scanning Colurimetry) thermo grams in different ranges were carried out at (R.T) heating rate = $100^\circ C/min$ (Linseis STA PT-1000) were run in Ibn-Haitham college for pure and applied sciences Ibn Al-Haitham. Ultra violet-visible spectrophotometer were recorded by using 1800 nm at Shimadzu department of chemistry, College of Science University of Baghdad. The electronic spectra of the compounds were measured in the region (200–800) nm by using (Varin Cary 100 Conc. UV-Vis). spectrophotometer at chemistry department, college of science, Mustansiriyah University. ^{13}C -NMR spectra were acquired in- $CDCl_3$ solution using a 300 MHz with tetra methyl silane (TMS) as an internal reference for 1H -NMR on Shimadzu were recorded at AL-al-Bait University-Amman, Jordan. Melting points were obtained by using (Melting point apparatus) on Gallen Kamp M, F, B 600-010f. TG at department of chemistry, College of science, university of Mustansiriyah. The FT-IR spectra were carried

out using Shimadzu FT-IR 8400S College of Sciences, University of Baghdad. The Biological activities were evaluated by measuring the diameter of inhibition zones(mm) by using Division Laminar flow clean Bench at College of education for pure Sciences, Ibn Al-Haitham, Baghdad University. All reagents and chemicals were commercially were used as received from suppliers. Para hydroxyl benzoic acid, butyl bromide sodium bicarbonate (fluka), Chloroform, hydrazine hydrate 90%, ethanol absolute, methanol, POCl₃, AgNO₃, CuCl₂.2H₂O, ZnCl₂, PdCl₂, H₂PtCl₆ and NiCl₂.6H₂O (Sigma Aldrich) and, PdCl₂ from (Riedel-dehien).(micro analysis Elemental) (C, H ,N and S) for ligand and their metal complexes were carried out on Elemental Analyzer (Euro EA 3000) Euro Victor Italy were recorded at College of Education for Pure Science (Ibn Al-Haitham) Baghdad University.

2.2. Synthesis

2.2.1. Synthesis of 4-(n-butyloxy) benzoic acid [S₁] and 4-(n-butyloxy) benzoate.[S₂]

The compounds [S₁ and S₂] were synthesis according to the method published in literature[12][13], scheme 1.

2.2.2. Synthesis of the [4- (n-butyloxy phenyl) hydrazide[S₃] and the primary ligand [L¹][2,5 bis(4- n -butyloxy phenyl) -1,3,4 oxadiazole

To the solution of precursor [S₂] (8g, 0.038mole) was dissolved in (35 ml) absolute ethanol, Then (10ml) hydrazine hydrate (90%) was added to the mixture then heated under reflux (10 hrs) dried and recrystallized from ethanol to give the precursor (S₃) [4- (n-butyloxy phenyl) hydrazide(yield75%) with melting point (155-157) °C[14], scheme 2. (5g, 0.029 mmole) of precursor (S₃) and (7g, 0.038 mmole) of (S₁) added (5ml) of POCl₃ solvent to the mixture then reflux for (2hrs). The precipitate formed washed with saturated solution of sodium bi carbonate filtered and dried to give pure of the ligand recrystallized from ethanol absolute to give the ligand[L¹] 2,5 bis(4- n-butyloxy phenyl) -1,3,4

oxadiazole(yield70%) with melting point (116-118 °C) [15], scheme 3.

2.2.3. Synthesis the compound (benzyl (propane-2- yl)carbamodithioate.

The secondary Ligand (benzyl (propane-2-yl)carbamodithioate) was synthesized according to the method published in literature[16], scheme 3.

2.2.4. Synthesis of Ag(L¹) complex

AgNO₃ (silver nitrate (0.17g, 1mole) was added to the (0.366g, 2mole) of primary ligand (L¹) in CH₂Cl₂ solvent. The mixture was stirred under dark and inert conditions at room temperature until the precipitate solid of AgNO₃ disappeared. The solvent was evaporated and the precipitate was collected and stored in desiccators after washed with a mixture of normal hexane and distilled then dried under vacuum yield (65%) with melting point 165 °C.

2.2.5. Synthesis of mixed ligand-Synthesis of [Cu (S-bpth) (L¹)₂] complex

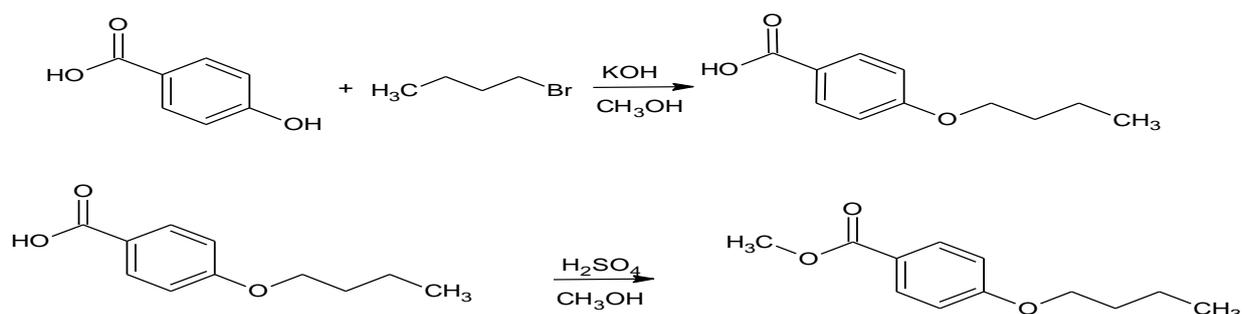
Mixed - ligand metal complexes by using ligand[L¹] as a primary ligand with sodium benzyl (propane-2-yl) carbamodithioate (S-bpth) as a co-ligand and Metal chloride (II) where M (II) = Ni(II), Pd(II), Pt(II), Cu (II) and Zn(II). A solution of (L¹) (0.366 g,2mmole) in di chloro methane (20ml) and (S-bpth) (0.245g,1m mole) was stirred for 15 min. Copper(II) chloride di hydrate salt (0.171g ,1mmole) was added. The mixture heated under reflux for 2 hrs. The Solid product washed with normal hexane and diethyl ether then dried to give green compound with melting point 267 °C, yield 60%.

(S-bpth)= Sodium benzyl (propane-2yl) carbamodithioate, scheme 5.

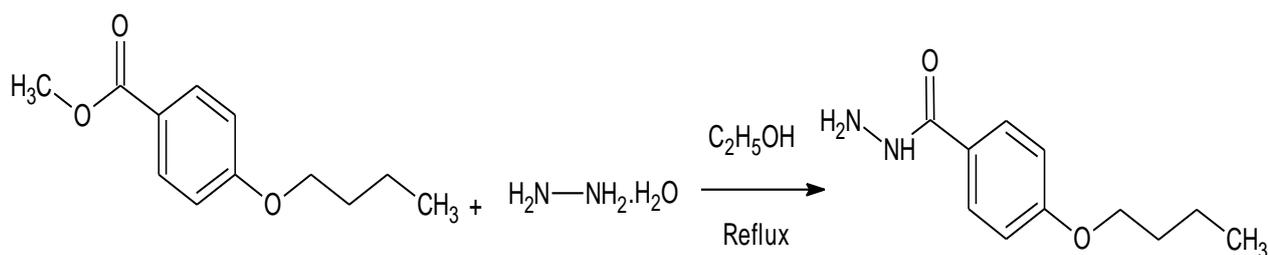
2.2.6. Synthesis of [pd(S-bpth)(L¹)₂]Cl, [pt(S-bpth)(L¹)₂]Cl, [Cu(S-bpth)(L¹)₂] and [Zn(S-bpth)(L¹)₂] complexes

A similar method to that performed for all mixed complexes was used except the weight of the metal salt which were used [0.237,

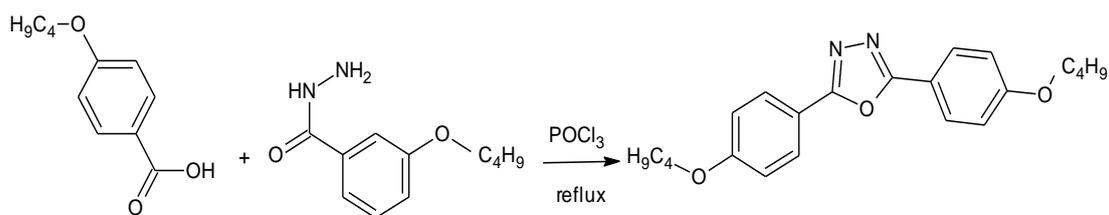
0.214, 0.302, 0.171 and 0.136 gm] below with the percentage, Table 1.



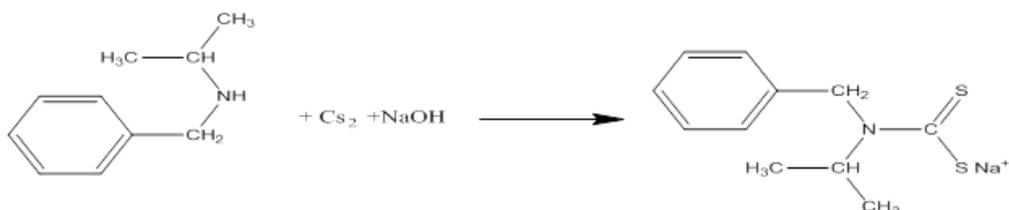
Scheme 1: Synthesis of 4-(n-butyloxy) benzoic acid [S₁] and 4-(n-butyloxy) benzoate.[S₂].



Scheme 2: synthesis of the n-(4-butyloxy) benzo hydrazide[S₃].



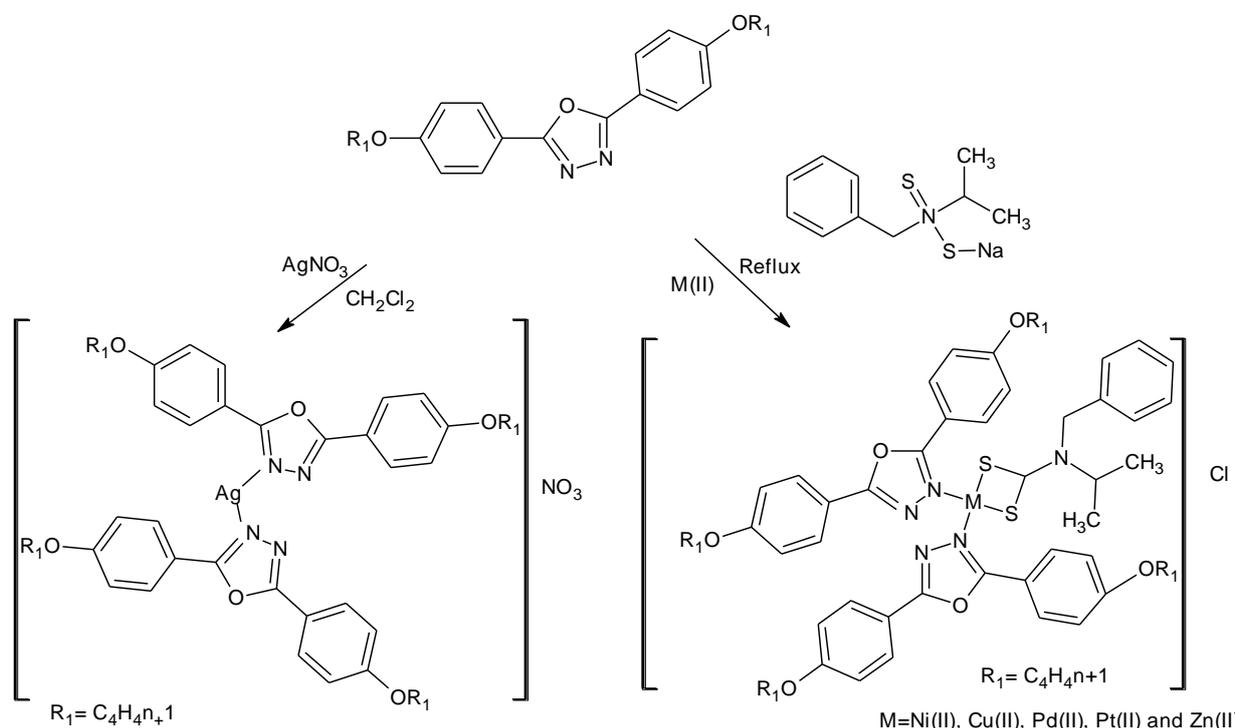
Scheme 3: Synthesis of the ligand [L¹] 2, 5 bis(4- n -butyloxy phenyl) -1,3,4 oxadiazole.



Scheme 4: Synthesis Sodium benzyl (propane-2-yl) carbamodithioate.

Table 1: Physical properties and elemental analysis of the prepared ligand and their mixed metal complexes.

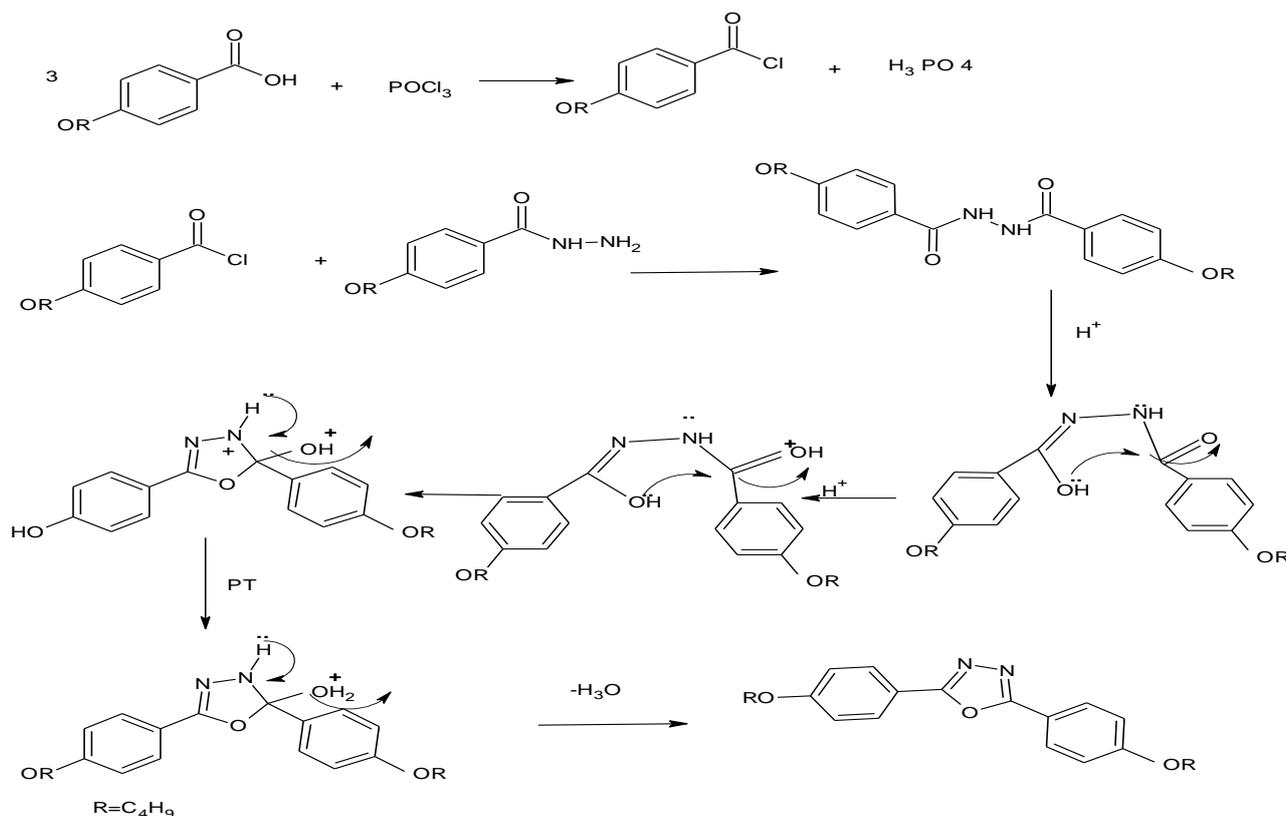
Comp.	Formula	Mwt g/mol	Yield %	Colour	m.p °C	Elemental analysis (found) calculate %				M
						C	H	N	S	
[S ₃]	C ₁₁ H ₁₆ N ₂ O ₂	208.25				(62.44) 63.44	(7.01) 7.74	(13.76) 13.45		
L ¹	C ₂₂ H ₂₆ N ₂ O ₃	366.45	70	Light Brown	116-118	(71.1) 72.11	(7.04) 7.15	(7.86) 7.64		
[Ag(L ¹) ₂]NO ₃	C ₄₄ H ₅₂ Ag N ₅ O ₉	902.77	65	Light Brown	165	(54.65) 58.54	(5.38) 5.81	(7.29) 7.76	-	(11.18) 11.95
[Ni(S-bpth)(L ¹) ₂]	C ₅₅ H ₆₆ Cl NiN ₅ O ₆	1050.41	60	Brown	188	(58.67) 62.83	(5.91) 6.33	(6.82) 6.66	(5.91) 6.01	(5.12) 5.58
[Pd(S-bpth)(L ¹) ₂]	C ₅₅ H ₆₆ ClPdN ₅ O ₆ S ₂	1099.14	70	Dark Brown	194	(60.02) 60.05	(6.62) 6.37	(6.81) 6.37	(5.13) 5.83	(9.09) 9.68
[Pt(S-bpth)(L ¹) ₂]	C ₅₅ H ₆₆ ClPtN ₅ O ₆ S ₂	1187.80	60	Deep Brown	220	(55.53) 55.60	(5.28) 5.60	(6.01) 5.90	(5.13) 5.40	(6.12) 6.42
[Cu(S-bpth)(L ¹) ₂]	C ₅₅ H ₆₆ ClCuN ₅ O ₆	1056.27	64	Green	290	(62.21) 62.54	(6.10) 6.30	(6.89) 6.63	(5.91) 6.07	(5.98) 6.02
[Zn(S-bpth)(L ¹) ₂]	C ₅₅ H ₆₆ ClZnN ₅ O ₆	1058	65	White	180	(62.27) 62.43	(6.11) 6.29	(6.82) 6.62	(5.89) 6.06	(6.02) 6.18



3. Result and Discuses

Reaction between 2,5-bis(4-butoxy phenyl) - 1,3,4- oxadiazole [S₁] with the precursor [S₃]

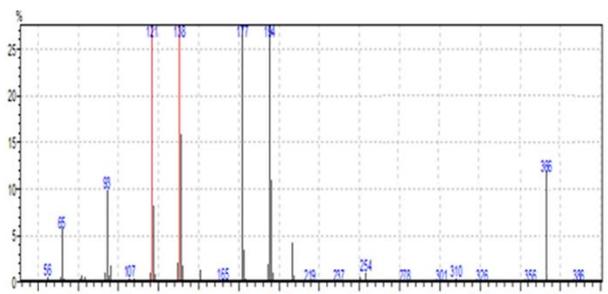
4-(n-butoxy) benzohydrazide in present of POCl₃ to obtained ligand [L¹] in good yield. Suggest mechanism, scheme 5.



Scheme 5: Suggested mechanism of [L1].

3.1. Mass spectra of the ligand

Figure 1 shows the mass spectrum of the (L^1) ligand. The high intensity peak around ($m/z = 366 M^+$) for ($C_{22}H_{26}N_2O_3$) conform the proposed structure of the prepared ligand. This fragment may indicate the formation of ligand [L^1] as the most stable species detected by the instrument requires 366, The other peaks detected at $M/Z=254, 194, 177, 134, 121, 93, 65$ correspond to [$C_{14}H_{10}N_2O_3$] $^+$ [$C_{10}H_{14}N_2O_2$] $^+$ [$C_9H_9N_2O_2$] $^+$ [C_8H_9O] $^+$ [C_6H_5O] $^+$ and [C_4OH] $^+$ respectively[17]. The proposed fragment ion pattern is out line in scheme 3.

Figure 1: Mass spectra of L^1 ligand.

3.2. 1H -NMR Spectrum of the ligand (L^1)

1H -NMR Spectrum of (L^1) in $CDCl_3$ displayed in Figure 2 appeared a triplet signal at ($\delta=0.96$ ppm, 6H) which assigned to protons of (C_{14} and C_{14}) equivalent to 6 protons, and a multiple that observed at the range ($\delta=1.33$ ppm, 4H) attributed to (C_{13} and C_{13}) which equivalent to 4 protons also multiple signal at ($\delta=1.71$ ppm) attributed to (C_{12} and C_{12}) which equivalent to 4 protons and a triplet signal showed at ($\delta=3.94$ ppm) attributed to (C_{11} and C_{11}) which equivalent to 4 protons a doublet signals at ($\delta=6.83$ ppm, 2H) ($\delta=6.83$ ppm, 2H) and ($\delta=7.37$ ppm, 2H) ($\delta=7.37$ ppm, 2H) the first signal attributed to the protons of (C_6 , C_{10} , C_6 and C_{10}) and the second signal attributed to the (C_5 , C_9 , C_5 and C_9) of the aromatic ring protons and at ($\delta=9.254$ ppm, 1H) attributed to the (N-H). these signals are good evidence to the formula of the ligand [2,5 bis (4-n-butyl oxy phenyl)-1,3,4-oxadiazole][18].

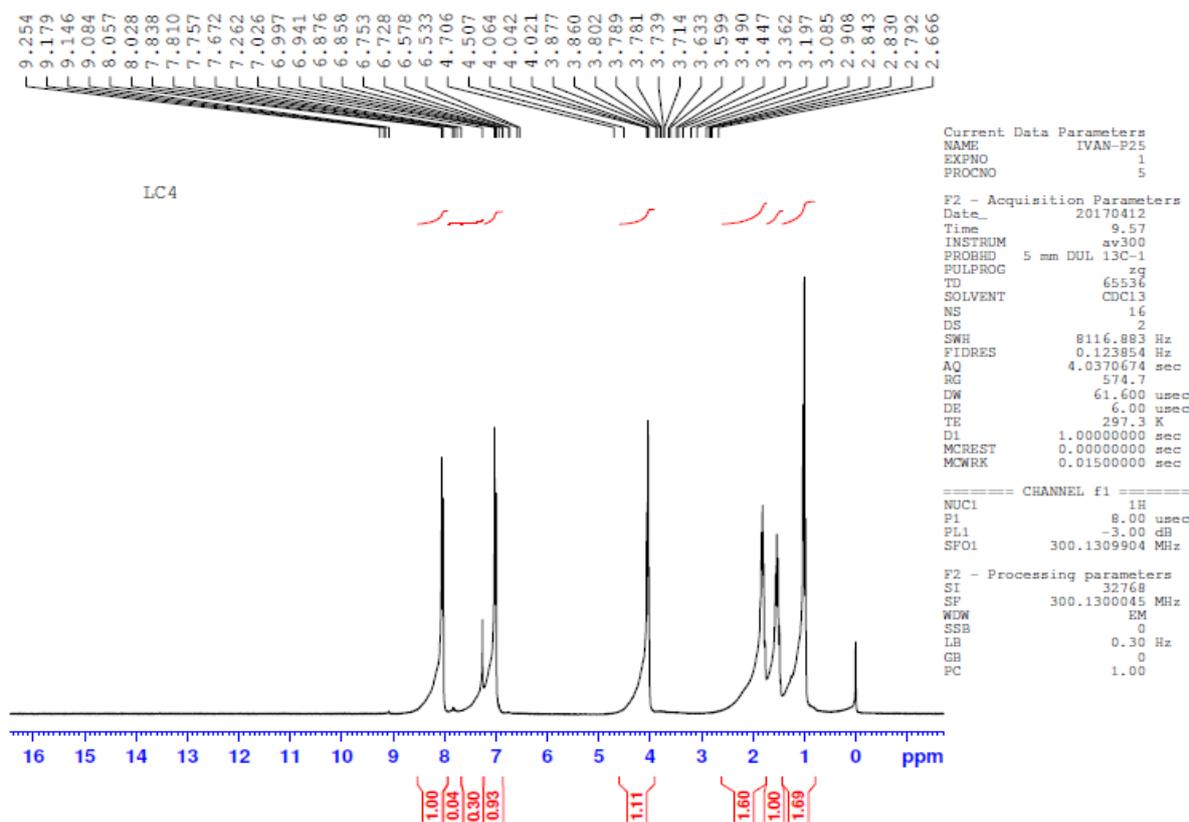


Figure 2: Proton- NMR spectra of L¹ in CDCl₃ solvent.

3.3. ¹³C-NMR Spectrum of the ligand (L¹)

¹³C- NMR spectrum for the ligand (L¹) in CDCl₃ is exhibited in Figure 3. The chemical shift at δ=13.830 ppm) due to (C₁₄ and C₁₄). The spectrum also showed signals at (δ =19.213-31.179 ppm) which assigned to (C₁₂-C₁₂) and (C₁₃-C₁₃) were assigned to the carbon atoms of the two hydrocarbon chains The

resonance at(δ =67.949 ppm) attributed to the (C₁₁ and C₁₁) carbon atoms. The chemical shift were observed at (δ=161.815ppm) attributed to the carbon of (C₃=N-N=C₃) the other signals that appeared in the range (δ=114.932-153.63ppm) due to the carbons of the aromatic ring.

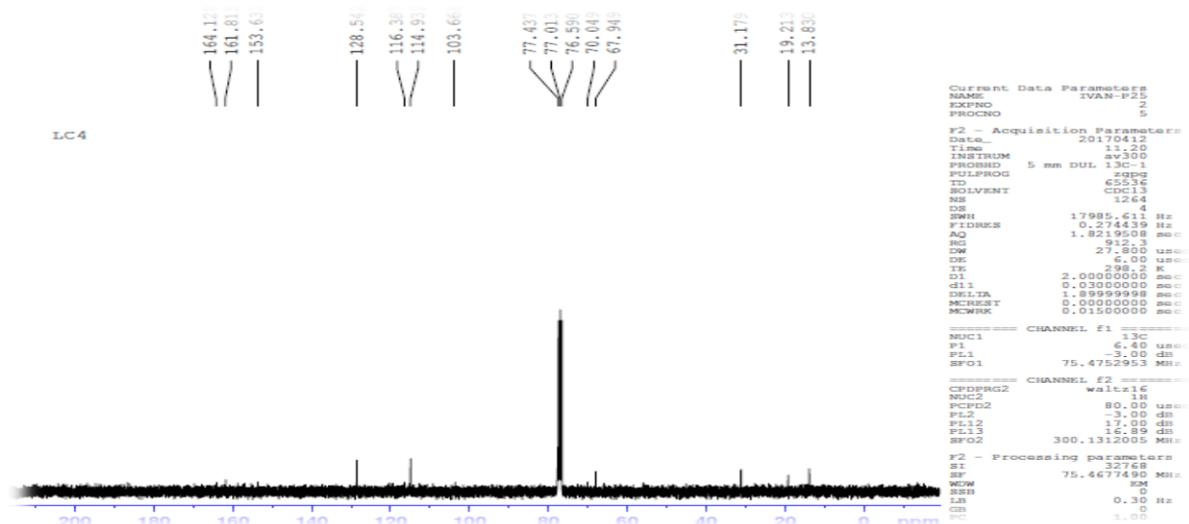


Figure 3: ¹³C- NMR spectra of [L¹] in CDCl₃ solvent.

3.4. FT-IR spectra of the ligand (L^1)

All the data of vibrational absorptions from FT-IR spectra for all organic and coordinated complexes are presented in Table 1. The FT-IR of this compound Figure 4 showed the bands at (2858-2872 cm^{-1}) are good evidence to

alkylation reaction. The band at (1608 cm^{-1}) attributed to the vibration of $\nu(\text{C}=\text{N})$ in addition the bands at (1249 and 1070 cm^{-1}) related to symmetrical and asymmetrical of (C-O-C) the band at (835) cm^{-1} due to ring

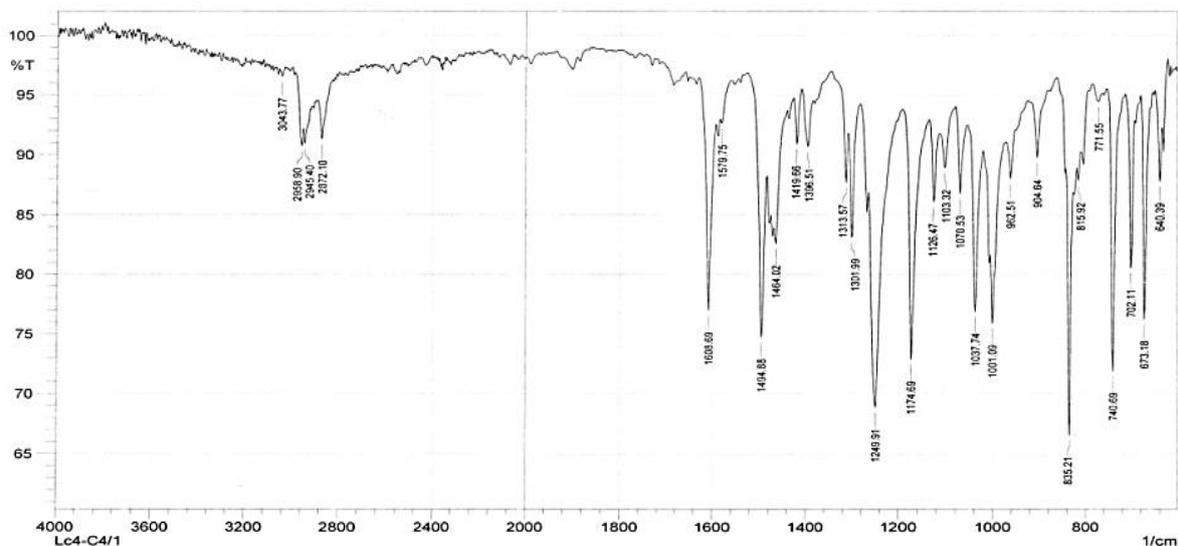


Figure 4: FT-IR spectral for (L^1) complex.

3.4.1. FT-IR spectral for $\text{Ag}(L^1)$ complex

The $\nu(\text{C}=\text{N})$ vibrations that showed in the spectra of free ligand, was found to be slightly shifted to a higher or lower frequencies in the spectra of $\text{Ag}(L^1)$ complex Figure 5. This

might give approve that the coordination of the ligand to the $\text{Ag}(\text{I})$ ion occurred through the nitrogen atom of the (C=N) group[19][20], Table 2.

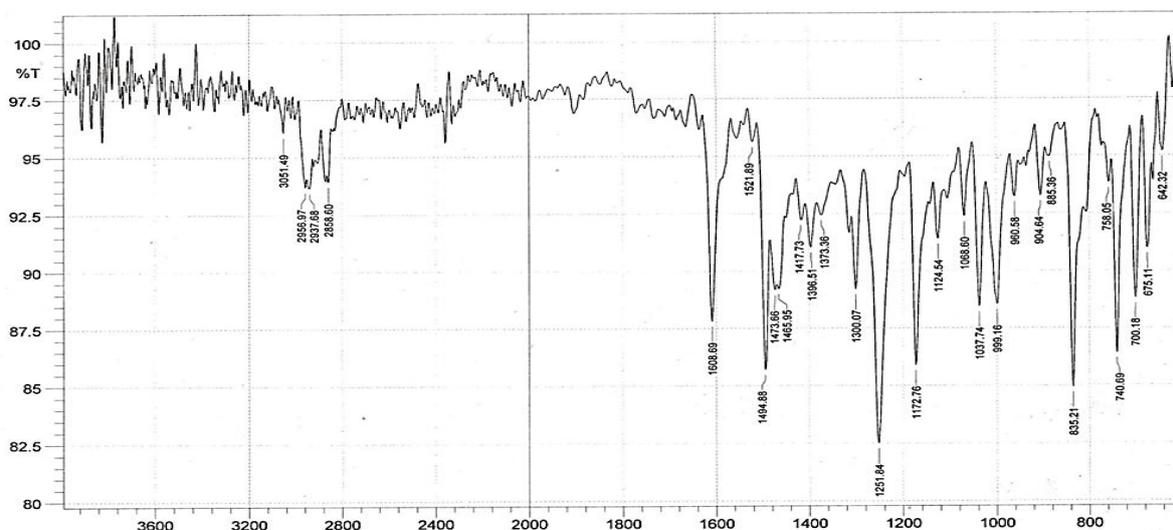


Figure 4: FT-IR spectral for $[\text{Ag}(L^1)_2]\text{NO}_3$ complex.

3.4.2. FT-IR spectral of Mixed-ligand (L^1) complexes

3.4.2.1. FT-IR spectra of $[Ni(S-bpth)(L^1)_2]Cl$ complex

The distinct absorptions from FT-IR spectra of the absorption synthesis complexes with (L^1) are listed in Table 1. The FT-IR spectrum of preparation the ligand (L^1) showed a bands related to $\nu(C=N)$ (C-O-C) of free ligand stretch at (1608 and 1249 cm^{-1}) respectively in the complexes the bands were shifted to a lower or higher frequencies comparison with the free ligand indicated to complex formation. The bands which detected at (1610 and 1253

cm^{-1}) in $[Ni(L^1)(S-bpth)Cl]$ complex[21] Figure 6. further bands which are attributed to $\nu(C-S)$ shifted to lower frequency and appeared at (1068) and (962) cm^{-1} [22] compared with that 1070 and 962 cm^{-1} in the free ligand. The FTIR of $Ni(L^1)$ complex exhibited band at 379 assigned to the $\nu(M-S)$. This results indicated to contribution of dithiocarbamato moieties in complexation from S atom as M-Sbond[23]. The FT-IR spectra $[Pd(bpth)(L^1)_2]Cl$ $[Pt(bpth(L^1)_2)C]$ $[Cu(Sbpth)(L^1)_2]Cl$ and $[Zn(S-bpt(L^1)_2)Cl]$ complexes are listed in Table 2.

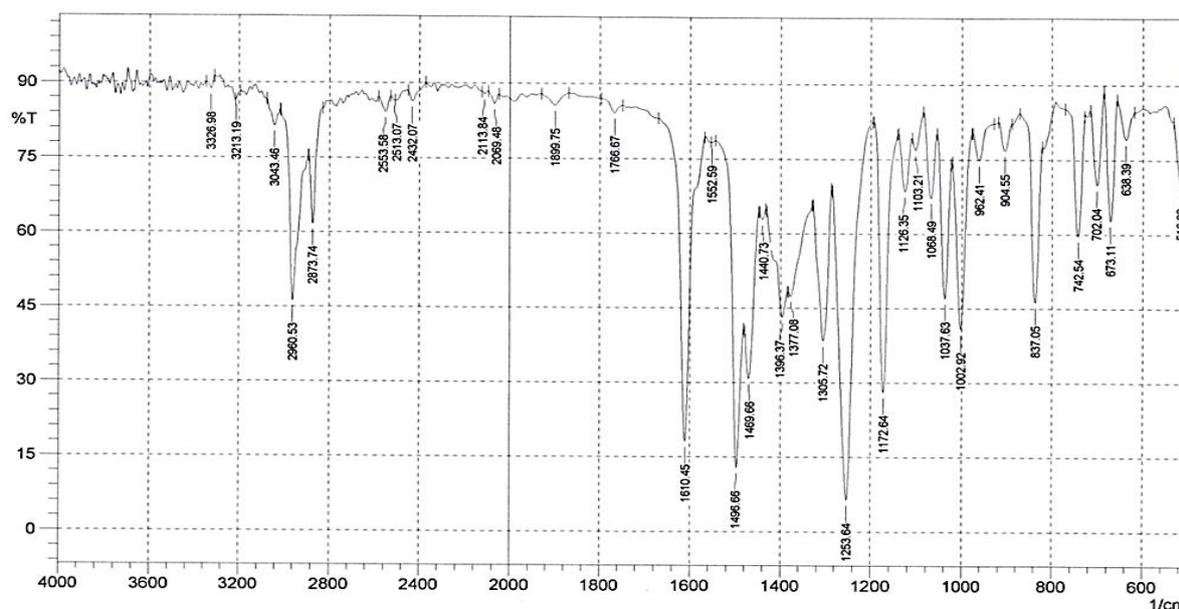


Figure 5: FT-IR spectra of $[pd(S-bpth)(L^1)_2]Cl$.

Table 2: FT-IR of mixed ligand (L^1) and $Ag(L^1)$ complexes.

Compound	$\nu(C-H)$ Arom	$\nu(C=N)$ cm^{-1}	$\nu(C=C)$ cm^{-1}	$\nu(C-O-C)$ cm^{-1}	$\nu(C-H)$ cm^{-1}	$\nu(C-S)$ cm^{-1}	$\nu(M-S)$ cm^{-1}	(C-H) Aliph.
$[(L^1)]$		1610		1249	1471	-	-	2924- 2868
$[Ag(L^1)_2]NO_3$	3068	1608	1500	1257	1469	-	381	2958 2873
$[Ni(S-bpth)(L^1)_2]Cl$	3043	1610	1496	1253	1469	1068 962	379	2960 2873
$[Pd(S-bpth)(L^1)_2]Cl$	3068	1608	1500	1257	1469	1072 906	381	2960- 2873
$[Pt(S-bpth)(L^1)_2]Cl$	3029	1608	1564	1255	1498	1068 898	383	2960- 2873
$[Cu(S-bpth)(L^1)_2]Cl$	-	1610	1552	1255	1498	1062 948	397	2931- 2869
$[Zn(S-bpth)(L^1)_2]Cl$	3068	1608	1500	1257	1496	1072 906	341	2958- 2873

3.5. UV-Visible spectra of the ligand [L^1] and [$Ag(L^1)$] complex.

The electronic absorption of the ligand [L^1] and their metal ion complexes were recorded in ethanol and DMSO at room temperature. The spectrum of [L^1] shows in Figure 6. The spectrum of the ligand exhibited a high intensity bands appeared in the region peaks at (245nm) (40816 cm^{-1}) ($9650\text{ molar}^{-1}\text{ cm}^{-1}$) and (248 nm) (40322 cm^{-1}) ($10060\text{ molar}^{-1}\text{ cm}^{-1}$) and (304 nm) (32895 cm^{-1}) ($26660\text{ molar}^{-1}\text{ cm}^{-1}$) assigned to ($\pi \rightarrow \pi^*$) ($n \rightarrow \pi^*$) respectively. The electronic spectrum of some complexes exhibited new bands with intensities and positions of these bands are mainly dependent on the ligand field effects stereo chemistry of complexes and electron configuration of the metal ion[24]. The absorption peaks of were summarized in Table 3. The UV-Vis spectrum of [$Ag(L^1)NO_3$] complex Figure 11, exhibited high intense absorption peaks at (253 nm) (39525 cm^{-1}) ($265\text{ molar}^{-1}\text{ cm}^{-1}$) (262 nm) (38167 cm^{-1}) ($383\text{ molar}^{-1}\text{ cm}^{-1}$) and (305 nm) (32786 cm^{-1}) ($806\text{ molar}^{-1}\text{ cm}^{-1}$) these absorption assigned to ligand field and charge transfer respectively since the metal ion belong to d^{10} system this metal do not show (d-d) transition therefore the stereochemistry for this complex liner around the ion $Ag^{+1(23)}$.

3.5.1 UV-Vis Spectra Data for [$Ni(S-bpth)(L^1)_2Cl$] [$Pd(S-bpth)(L^1)_2Cl$] and [$Pt(bpth)(L^1)_2Cl$] complexes.

The absorption of [$Ni(S-bpth)(L^1)_2Cl$] and [$(Pt)(S-bpth)(L^1)_2$] complexes were listed in Table 3. The electronic spectrum of Ni(II) complex Figure 7 exhibited the absorption peak at 258 nm (38766 cm^{-1}) ($12510\text{ molar}^{-1}\text{ cm}^{-1}$) due to ligand field other peaks at 349 nm (28653 cm^{-1}) ($350\text{ molar}^{-1}\text{ cm}^{-1}$) and 5617699 cm^{-1} ($1920\text{ molar}^{-1}\text{ cm}^{-1}$) were assigned to electronic transition type $3T_{1(F)} \rightarrow 3A_{1(F)}$ and $3T_{1(F)} \rightarrow 3T_{1(F)}$ respectively indicating tetrahedral geometry around the Ni^{+2} ion[24]. The electronic spectrum of Pt(II) complex Figure 8 exhibited the absorption peaks at 257 nm (38911 cm^{-1}) ($594\text{ molar}^{-1}\text{ cm}^{-1}$) 312 nm (32051 cm^{-1}) ($665\text{ molar}^{-1}\text{ cm}^{-1}$) and 387 nm ($25839\text{ molar}^{-1}\text{ cm}^{-1}$) ($1318\text{ molar}^{-1}\text{ cm}^{-1}$). Peaks due to ligand field and third peak attributed to $^1A_{1g} \rightarrow ^1B_{2g}$

transitions this peaks were indicated a square planar geometry about the Pt^{+2} ions[24][25]. According to the magnetic moment values, all complexes are diamagnetic except Zn(II) complex because of d^8 of Ni(II) Pd(II) and Pt(II) that low spin. While Zn (II) complex has filled d-orbital. The molar conductivity value of all complexes was measured in DMSO as a solvent at concentration of 10^{-4} M at room temperature. The values of the molar conductance of the complexes lied in the range ($22\text{-}40\text{ }\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$). These results indicated that electrolyte complexes. All the chloride anions are non-coordination to the metal (outside the coordination sphere).

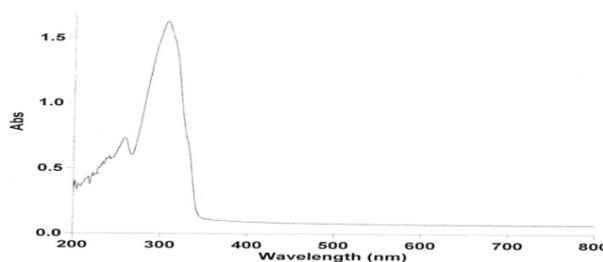


Figure 6: Electronic spectrum of L^1 .

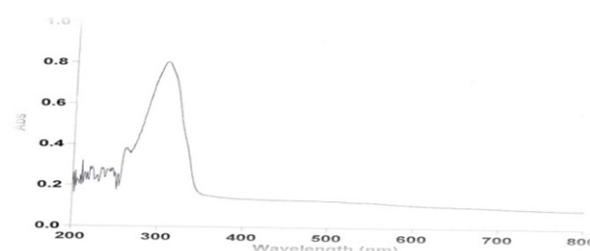


Figure 7: Electronic spectrum of $Pd(S-bpth)(L^1)_2Cl$.

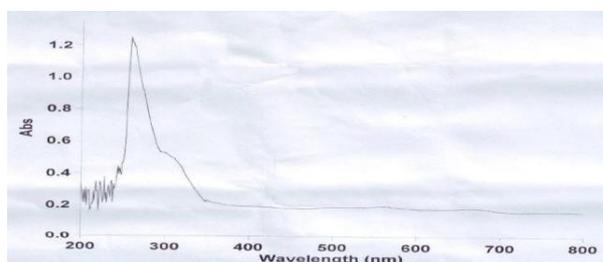


Figure 8: Electronic spectrum of $[Ni(S-bpth)(L^1)_2]Cl$.

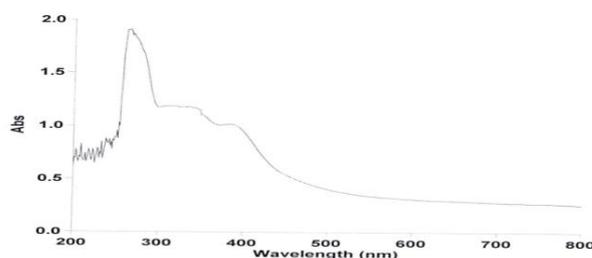


Figure 9: Electronic spectrum of $Cu(S-bpth)(L^1)_2Cl$.

Table 3: UV-Visible absorptions, molar conductivity and magnetic moments of the prepared complexes.

Compound	λ max nm	Wave number ν .cm ⁻¹	ϵ dm ³ .mol ⁻¹ .cm ⁻¹	Assignment	Suggested Geometry	Δm Ω^{-1} .cm ² .mol ⁻¹	μ B.M.
[(L ¹)]	245	40816	9560	$\pi \rightarrow \pi^*$			
	304	32895	26660	$n \rightarrow \pi^*$			
[Ag(L ¹) ₂]NO ₃	253	39525	256	$\pi \rightarrow \pi^*$	Linear	20	
	262	38167	383	$n \rightarrow \pi^*$			
	305	32786	806	C.T			
[Ni(S-bpth)(L ¹) ₂]Cl	258	38760	12510	$\pi \rightarrow \pi^*$	Tetrahedral	31.5	2.75
	349	28653	2320	${}^3T_1 \rightarrow {}^3T_1(P)$			
	565	17699	1920	${}^3T_1 \rightarrow {}^3T_1(P)$			
[Pd(S-bpth)(L ¹) ₂]Cl	250	40000	729	$\pi \rightarrow \pi^*$	Square planar	31.4	Diamagnetic
	282	35461	35	$n \rightarrow \pi^*$			
	442	22624	34	${}^1A_{1g} \rightarrow {}^1B_{1g}$			
[Pt(S-bpth)(L ¹) ₂]Cl	257	38911	594	$\pi \rightarrow \pi^*$	Square planar	30.5	Diamagnetic
	312	32051	665	$n \rightarrow \pi^*$			
	387	25839	1318	${}^1A_{1g} \rightarrow {}^1B_{2g}$			
[CuS-bpth)(L ¹) ₂]Cl	268	37313	1155	$\pi \rightarrow \pi^*$	Distorted Square planar	306	1.68
	309	32363	1168	$n \rightarrow \pi^*$			
	398	25126	1018	$B_{1g} \rightarrow B_{2g}^2$			
[Zn(S-bpth)(L ¹) ₂]Cl	203	49261	1046	$\pi \rightarrow \pi^*$	Tetrahedral	38.7	Diamagnetic
	245	40816	1966	$\pi \rightarrow \pi^*$			
	304	32895	1155	C.T			

3.6. Thermal analysis

3.6.1. Thermal decomposition of (L¹)

The thermo analysis of [L¹] is showed in Figure 10 at temperature range (50-594.4 °C). The thermo gram curve indicated to one decomposition step. The TGA peak observed at 594.4 °C indicated the loss (C₂₀H₂₆O₂) fragment (det.= 9.77 mg, 83.0457 %, calc.=9.93 mg). The final residue of the ligand recorded above 600 °C assigned to the (det.=2.33 mg, 16.945 %, calc.=2.07 mg) attributed to the [C₂N₂O] peak at 115.6 °C refer to exothermic decomposition processes .^(25,26) the results are listed in Table 5.

3.6.2. Thermal decomposition of [Ag(L¹)] [Cu(S-bpth)(L¹)₂]Cl, [Pd(S-bpth)(L¹)₂]Cl, and [Pt(S-bpth)(L¹)₂]Cl

The thermo gram of [Ag(L¹)] is shown in Figure 13. Which indicates the Ag(L¹) complex. The TGA peak recorded at 256.403 °C assigned to the loss of (C₈H₁₆NO₃) (det.=2.89 mg, 19.32 %, calc.=2.89 mg). The second step recorded at 587.8 °C account for the loss of (C₁₃ H₁₈ O₄) portions (det.=4.80 mg, 32.09 %, calc.= 4.89 mg) The third step recorded at 595 °C account for the loss [C₂O₂H₇] (det.=1.56 mg, 10.53 %, calc.=1.57

mg). The differences between the observed and calculated may be related To sublimation process, the final residue of the complex recorded above 600 °C is attributed to the [Ag and C₂₂H₁₆N₄] (obs.=5.77 mg, 56.06 %, calc.=5.47 mg). The DSC curve indicated endothermic decomposition processes at temperature 595 °C while peaks at 237 °C and 237 °C refer to exothermic decomposition processes. The exothermic peaks may be indicate combustion of the organic ligand in an argon atmosphere[26][27]. The results are listed in Table 5. The thermo gram of [Cu(L¹)] is shown in Figure 14. The TGA peak recorded at 459.92 °C assigned to the loss of (C₅H₆₆S O₄ and N) (det.=14.17 mg, 74.90%, calc.=14.2 mg). The differences between the observed and calculated may be related to sublimation process. The second step occurred at 587.83 °C account for the loss of (C-O) portions (det.=1.98mg, 8.39%, calc.=1.55mg). The final residue of the complex recorded above600 °C assigned to the (obs.=3.28mg16.71 % calc.=2.82mg) attributed to(Cu and C₃N₄O₂S Cl). The DSC curve indicated exothermic decomposition processes at temperature at 115, 404 and 506 °C refer to exothermic decomposition processes .The endothermic and peak may be indicate



combustion of the organic ligand in an argon atmosphere. The thermal decomposition data of the ligand (L^1) and some mixed metal complexes are listed in Table 5.

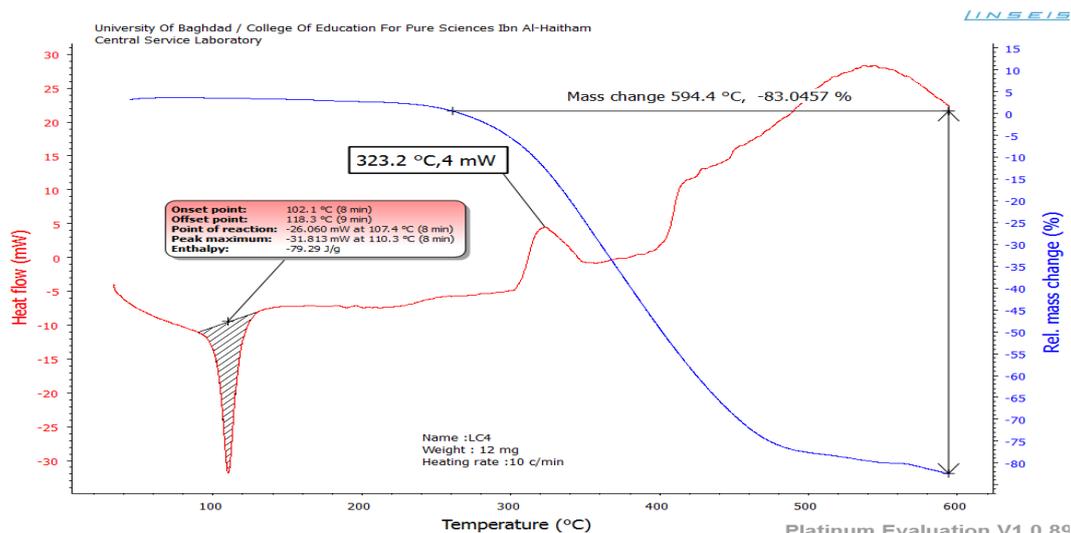


Figure 10: (TG/DTG and DSC) Thermo gram of $[(L^1)]$ in argon atmosphere.

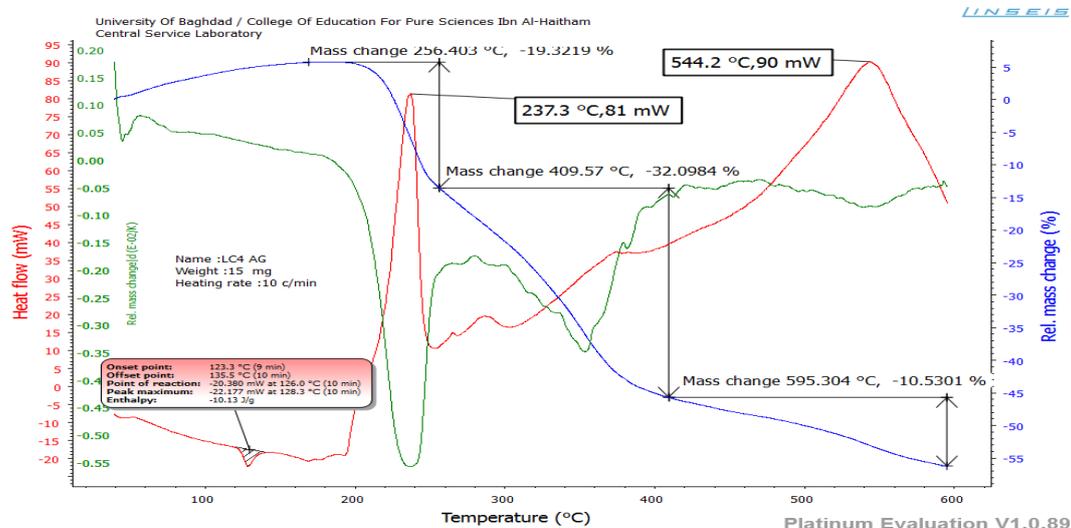


Figure 11: (TG/DTG and DSC) Thermo gram of $[Ag(L^1)]$ in argon atmosphere.

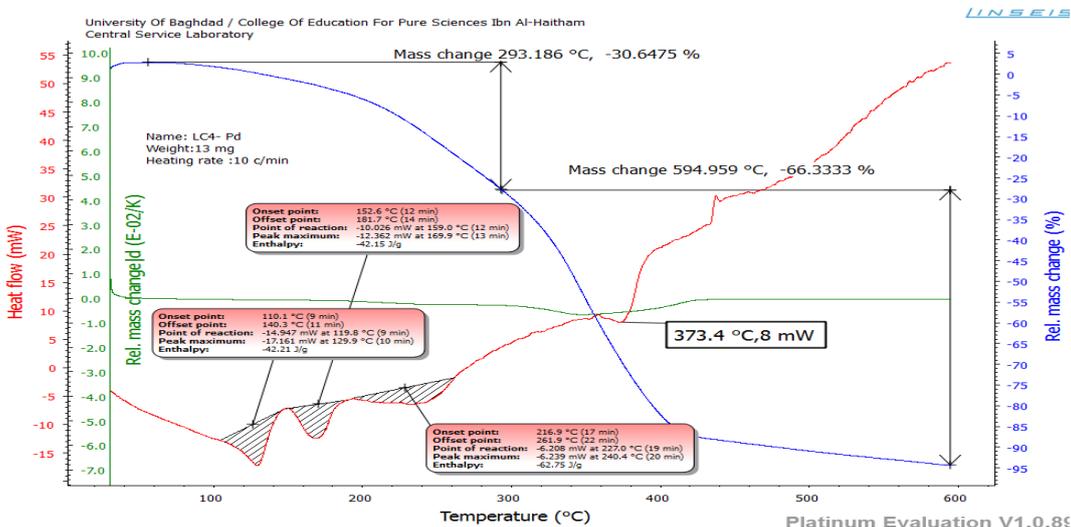


Figure 12: (TG/DTG and DSC) Thermo gram of $[pd(L^1)]$ in argon atmosphere.

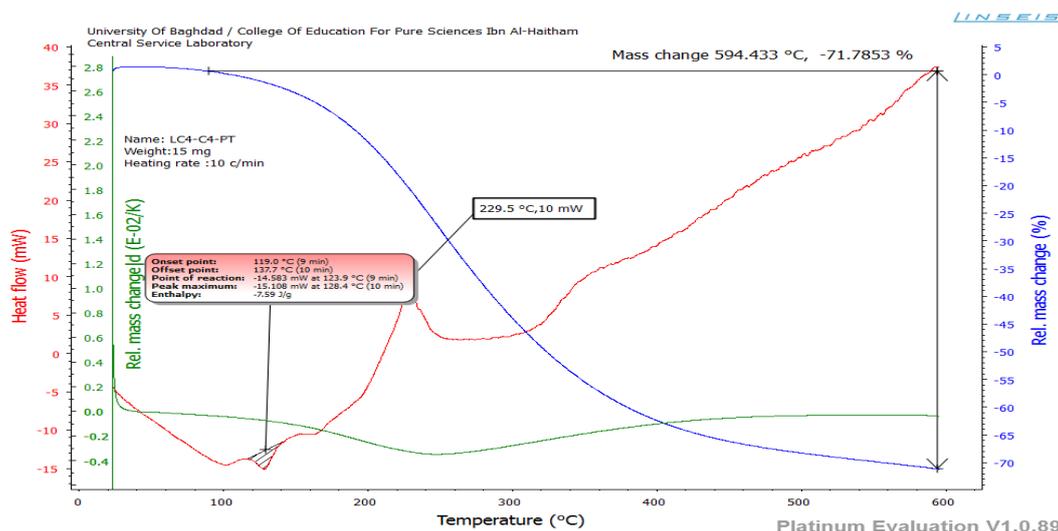


Figure 13: (TG/DTG and DSC) Thermo gram of [Pt(L¹)] in argon atmosphere.

Table 4: TGA/DTG/DSC data for some [L¹]complexes.

Compound	Decomposition Step	TG/DTG Temperature	Removes Species	Wt. loss (Calc.)	Wt. Found
[L ¹]	1 st (Residue)	594.4 600	(C ₂₀ H ₂₆ O ₂) (C ₂ N ₂ O ₂)	9.96 2.03	9.77 2.33
[Cu(L ¹)]	1 st 2 nd Residue	459.92 587.83 600	(C ₅₁ H ₆₆ SO ₄ and N) (C-N) (C ₃ N ₃ O ₂ SCI and Cu)	14.2 1.55 3.17	14.17 1.98 3.28
[Pt(L ¹)]	1 st (Residue)	594.3 600	(C ₅₁ H ₆₂ NO ₄ S ₂ Cl) (C ₄ H ₄ O ₂ N ₄ and Pt)	10.70 4.3	10.77 4.22
[Ag(L ₁) ₂]NO ₃	1 st 2 nd 3 rd Residue	256.403 587.83 595.304 Up 600	(C ₈ H ₁₆ NO ₃) (C ₁₃ H ₁₃ O ₄) (C ₂ H ₇ O ₂) (C ₂₂ H ₁₆ N ₄ and Ag)	2.89 4.89 1.57 5.47	2.89 4.80 1.56 5.77
[Pd(L ¹)]	1st 2 nd Residue	293.18 594.95 Up 600	(C ₂₃ H ₂₈ O ₂) (C ₂₆ H ₃₀ O ₃ NS ₂ Cl) (C ₆ H ₈ N ₄ O and Pd)	4.021 8.61 0.41	3.97 8.54 0.49

3.7. Biological Activity

Study of anti-bacterial activity for the mixed ligand complexes

The anti-bacterial activity for the mixed-ligand complexes were studied against four types of bacteria like staphylococcus aurea, Bcillusubtilis, Esherichia coli and Eterobactern were shown in Figure 13. Results indicated that (Ag 10⁻⁴) ppm and (Cu 10⁻⁴) ppm complexes were more active against all kinds of bacteria and (Cu 10⁻⁴) ppm was inactive against three kinds of bacteria ⁽²⁷⁾. The mixed ligand complexes are generally stable in the DMSO solvent so that used as a biological solvent media because of the stability of

compounds in this solvent and its negative effect against studied bacteria, DMSO was selected as solvent media for the biological tests. The ampicillin and Ciprofloxacin are used as a control for bacteria. The data of the mixed ligand complexes at concentration of 5 ppm, 3 ppm, and 2ppm should be discuses against Bacillus subtilis, Staphylococcus aureus, Escherichia Coli and Eterobactern. The antibacterial activity of (L¹) complexes showed the order [Ag(L¹)₂No₃] > [Cu(L¹)₂(s-bpth)Cl] > [Pt (L¹)₂ (s-bpth) Cl] > [Pd(L¹)₂(s-bpth)Cl] was found to [Ag(L¹)₂No₃] had the best effect on it against Bacillus subtilis,

Staphylococcus aureus, Escherichia Coli and Eterobactern. The results are listed in Table 5.

Table 5: Bacterial activity of L1 complexes

Compound	Staphylococcus Aureu	Bacillus subtilis	Eterobactern	Escherichia Coli
D1*	22mm	23mm	10mm	-
D2**	19mm	23mm	-	-
Pt 10 ⁻³	-	14mm	12mm	-
Pd 10 ⁻³	13mm	12mm	12mm	-
Ag 10 ⁻³	18mm	20mm	11mm	-
Cu 10 ⁻⁴	19mm	26mm	12mm	13mm
Pt 10 ⁻³	-	-	-	14mm
Pd 10 ⁻⁴	16mm	15mm	10mm	-
Ag 10 ⁻⁴	20mm	16mm	20mm	23mm
Cu 10 ⁻⁴	-	10mm	-	-

* D1= Ampicline, ** D2= Ciprofloxacin

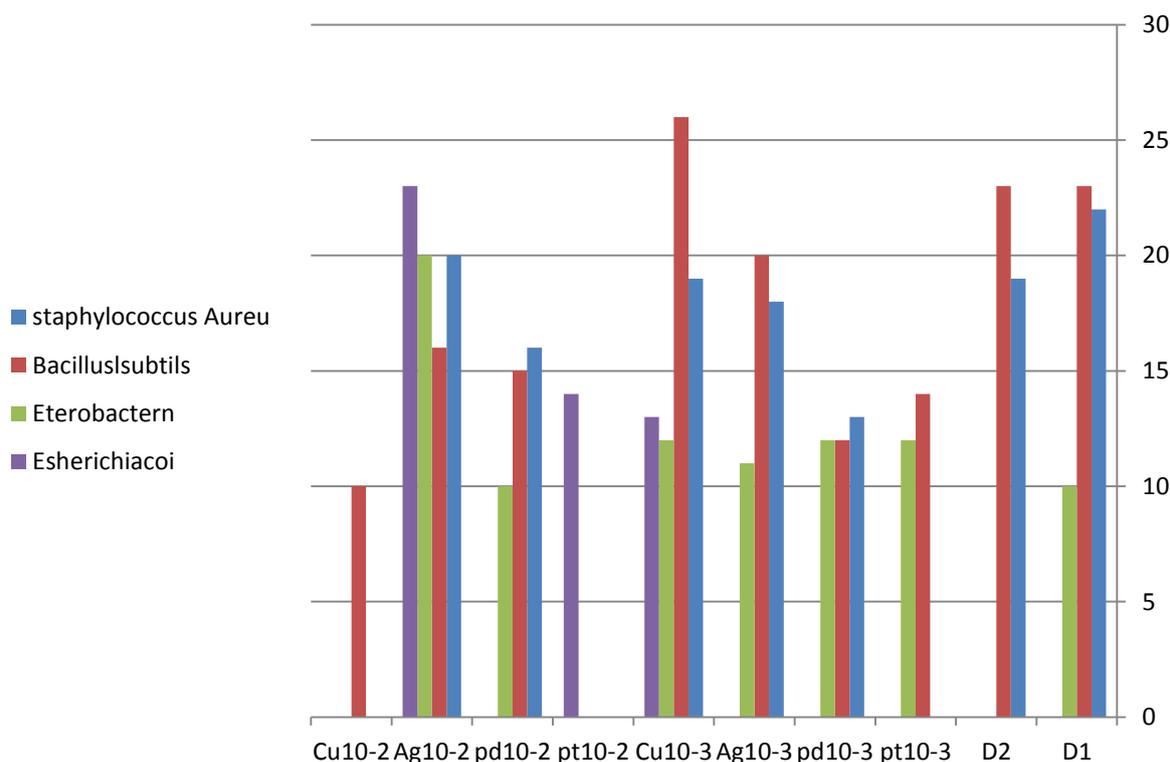


Figure 14: Evolution of diameter zone (mm) of inhibition of L¹ complexes against growth of bacterial strains.

Conclusion

This paper reports the synthesis, spectral and characterization of the ligand 2,5 bis(4- n - butyloxy phenyl) -1,3,4 oxadiazole and its complexes $[M(S-bpth)(L^1)_2]Cl$ where M (II) = Ni(II) Pd(II) Pt(II) Cu(II) and Zn (II).

S-bpth=(benzyl (propane-2-yl)carbamodithioate), containing en as the co-ligand. The structural characterization of the complexes was established on the basis of the

techniques, IR spectra, UV-Vis spectroscopic, and some of complexes by Thermal analysis. It was found that Natom and S-atom of thion group is coordinated to the metal in all cases. Furthermore the biological evaluation of the ligands, and their metal complexes in control DMSO with certain suitable concentrations of 10-20 ppm proved the high activity against some selected bacteria then leads to future using in the pharmaceutical industry. The complexes showed biological activity against

bacteria strains Staphylococcus aureus, Bacillus subtilis, Escherichia Coli and eterobactern .

References

- [1] V. Subbaiah DRCV, Mahesh K and Lakshmi, TR. "Synthesis of and bioassay of amino-pyrazole, aminoisoxazolonand amino-pyrimidinone derivatives" *Chem PharmBull*, 55, 1704-1709, (2007).
- [2] Bazgir, A., Khanaposhtani, M. M. and Sooski, A. A., "One pot synthesis and antibacterial pyrazolo[4',3':5,6]pyrido[2,3-d]pyrimidine-dione derivatives" *BioorgMed ChemLett*, 18, 5800-5803, (2008).
- [3] Shinde DB, Aaglawe MJ, Dhule SS, Bahekar SS and Wakte PS. "Synthesis & antibacterial activity of some oxazolone derivatives" *J KorChem*, 47, 133-136, (2003).
- [4] Achson A. "An introduction to the chemistry of heterocyclic compounds", Willy-Intersciences, India, 3rd ed., (2009).
- [5] Loetchutin, C. Chau, F. Mankhetkorn, S. "Synthesis and evaluation of 5-aryl-3-(4-hydroxyphenyl)-1, 3, 4-oxadiazole-2-(3H)-thiones as P-glycoprotein inhibitors" *Chemical and pharmaceutical bulletin*, 51 (6), 728-730, (2003).
- [6] "Potent anticancer agents. Bioorganic & medicinal chemistry letters", 19 (15), 4492-4494, (2009).
- [7] Revaansiddappa, B. C. and 7-7-Subrahmanyam E. V., *Int. J. Chem. Tech. Res*, 2, No.2, pp. 1094 - 1096, (2010).
- [8] Kumar, D.; Sundaree, S. Johnson, E. O. Shah, K., "An efficient synthesis and biological study of novel indolyl-1, 3, 4-oxadiazoles as 71".
- [9] Dawood Z. F., Mohammed T. J. and Sharif M. R., *IJVS*, 2009; 23(Supplement II):135-141.
- [10] Balaramesh P., Abdul Jabbar A. and Venkatesh P., *ijspr*, 2014; 4(5):1-7.
- [11] Balaramesh P., Venkatesh P., Abdul Jabbar A., *IJRSET*, 2014; 3(8):15301-15309.
- [12] Kasture V. S. Katti S. A., Mahajan D., Wagh R., Mohan M. and KSB. *Pharmacol Online*, 1, 385 - 395, (2009).
- [13] Mahajan S. K. Dr. Chaudhari R. Y. WRS. *J Pharm Res*, 4(7), 2285 - 2287, (2011).
- [14] Mandal S., Saha D., Jain B. and JVK, *Int J ResPharmaBiomedSci*, 2(1), (2011).
- [15] Subramani A. K., Kaliapan I., Bairam R. and NR, *DerPharmaChemica*, 1(1), 70-77, (2009).
- [16] Vocels B. P., "Text Book of Partical organic Chemistry", Ed 5 p(902).
- [17] Porter QN., "Mass Spectroscopy of heterocyclic compounds", 2nd ed., Wiley, New Yourk., p 883. 1985.
- [18] Browne M., Burnett D.A., Calpen M.A., Chen L.Y., Calder J.W., Domalski M., Dugar S., Pushpavanam P., Sher R., Vaccaro W., Visiano M. and Zhao H., *Tetrahedron Lett*, 36 (35), 2555, (1995).
- [19] Denes Nemcsok, Attila Kovacs KMS and VML., "Vibrational spectroscopic and theoretical study of 3,5-dimethyl-1-thiocarboxamide pyrazole(L) and the complexes Co and Cu." *ChemPhys*, 328, 85-92, (2006).
- [20] Nakamoto. "Infrared and raman spectra of inorganic and coordination compounds." Wiley Interscience, New York, (1997).
- [21] M. J. Al-Jeebori, A. A. Ameer and N. A. Boud, "Novel Pentadentate Ligand of N3 S2 Donor Atoms and Its' Complexes With (Ni, Co, Cu, Fe, Hg, Ag, and Re)", *J Ibn Al-Haitham Pure Appl. Sci.*, 17, 3, 80, (2004).
- [22] Carolin SH and AM, *Baghdad Sci J*. 9(4), 668-679, (2012).
- [23] Bonati F. and Ugo R. J. *Organomet Chem*, 10:257-268, (1967).
- [24] Lever A. B. P. E. "Inorganic Electronic Spectroscopy", levier Science Publishers, 1984; 2nd Ed., A.B.E, 2nd Ed, 161, (1984).
- [25] S. Marguet, D. Markovitsi, P. Millie, H. Sigal and S. Kumar, *J. Phys. Chem. B*, 102, 4697, (1998).
- [26] E.I. Yousif, H. A. Hassan, R. M. Ahmad MJA-J", "Formation of macrocyclic complexes with bis(dithiocarbamate) ligands: Synthesis, spectral characterization and bacterial activity", *Der Chem Sin*, 53-65, (2016).
- [27] T. H. Muat M. A., "phenoxo and azido-bridged complexes with N₂OS₂ Schiff-base ligand: Synthesis, spectral investigation and bacterial activity", 2, 156-171, (2016).
- [28] Joseph A. Lemire, Joe J. Harrison R and JT. "Antimicrobial activity of metals: mechanisms, Molec.Targ.