

Synthesis and Characterization of [1-phenyl-3-naphthoyl-2-thiourea] and Its Metal Complexes with [Co (II), Ni (II), Cu (II), Zn (II), and Cd (II)] ions and Study Antibacterial Activity and Corrosion Inhibitor

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Abstract

The formation of Co (II), Ni (II), Cu (II), Zn (II) and Cd (II)-complexes (C₁-C₅) respectively were studied with new thiourea ligand [1-phenyl-3-naphthoyl-2-thiourea] from 2-naphthoic acid in three steps. The suggested structures of the ligand and its complexes have been determined by using C.H.N.S analyzer, thermal analysis, FT-IR, U.V-Visible, ¹HNMR, ¹³CNMR, conductivity measurement, magnetic susceptibility, and atomic absorption. According to these studies, the ligand coordinates as a bidentate with metal ions through oxygen atom of carbonyl, and sulfur atom of thione and the ratio of metal to ligand (M:L) as (1:2) and all the complexes were octahedral structures except copper-complex was distorted octahedral structure

Keywords: Thiourea ligand, antibacterial activity, Corrosion inhibitor.

Introduction

Thiourea (TU) is the analogue compound to urea with replacement of oxygen atom in urea by sulphur atom, the properties of urea and thiourea differ significantly because of the difference in electronegativity between sulfur and oxygen atoms [1]. It has been observed that the reactivity of di- and tri-functionalized compounds containing hetero atoms like oxygen, nitrogen, and sulfur [2].

Thiourea and its derivatives represent a well-known important group of organic compounds due to the diverse application in fields such as medicine, agriculture, coordination and analytical chemistry [3]. The metal complexes of thiourea are neutral and their colors vary with the nature of the metal ions [4]. This paper reports the synthesis and characterization of new thiourea derivative ligand derived from 2-naphthoic acid and its complexes with Co (II),

Ni (II), Cu (II), Zn (II) and Cd (II).

Experimental

Synthesis of thiourea ligand [1-phenyl-3-naphthoyl-2-thiourea]

The methods for preparation this ligand by three steps:

Synthesis of 2-naphthoyl Chloride

In a round-bottom flask equipped with condenser and drying tube is added a solution of 2-naphthoic acid (0.86 g, 0.005 mol) in anhydrous 1,2-dichloroethane(11ml) and thionyl chloride (0.7 mL, 0.01mol) is added. The mixture is refluxed for 3 hours. The solvent and the excess thionyl chloride are removed under vacuum distillation the white product formed (yield 80%, mp 48 °C) [5].As shown in the Scheme (1).

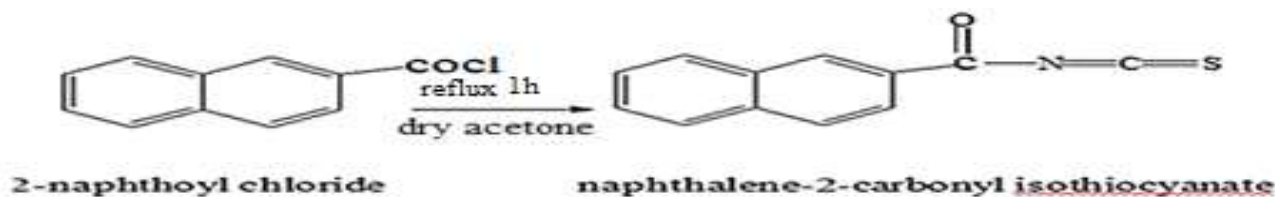


Scheme 1:

Synthesis of naphthalene-2-carbonyl isothiocyanate

The raw obtained 2-naphthoyl chloride (0.381 g, 0.002mol) is dissolved in anhydrous acetone (15 ml) and added to a solution of

ammonium thiocyanate (0.194 g, 0.002mol) in dry acetone. The reaction mixture is refluxed one hour in a round-bottom flask equipped with condenser and drying tube (mp 68 °C) [5], as shown in the Scheme (2).

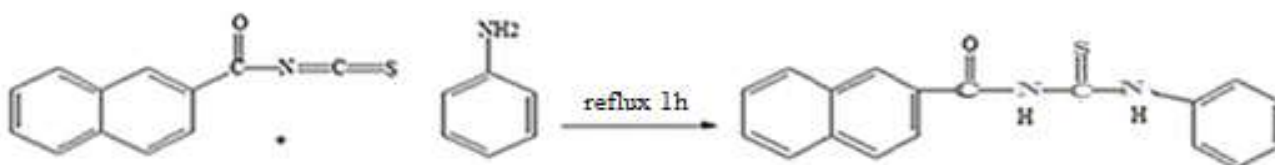


Scheme 2

Synthesis of ligand [L]

A solution of the suitable aniline (0.54ml, 0.006mol) dissolved in anhydrous acetone is added while stirring to the naphthalene -2-carbonyl carbonyl isothiocyanate solution(0.006mol, 1.278gm). The mixture is

heated under reflux for one hour and afterwards poured into ten times its volume of cold water when the 1-phenyl-3-naphthoyl-2-thiourea precipitated was filtered and washed in ethanol (yield 67%, m.p 136-138 °C) [5], as shown in the Scheme(3).



Scheme 3:

Synthesis of Complexes [C₁-C₅]

A solution of metal acetate (0.0001 mole that soluble in 7ml of ethanol 99% in all ion salts except copper salt 0.00005 mole of copper acetate that soluble in 7ml of ethanol) (0.0248 gm, 0.0212 gm, 0.0108gm, 0.0219gm, 0.0266gm in the (C₁-C₅) respectively is added drop wise to a solution of ligand (0.0002mol, 0.0612gm that soluble in 14ml of ethanol 99%) then the mixture refluxed for (12h for C₁,C₂ , 1h after that stirring for 24h in the C₃, and 6h in the C₄,C₅) then the mixture lifted overnight ,the products were filtered and wash in ethanol and dry in desiccator overnight[6] .

were defined for the ligand(L)and its complexes (C₁,C₂,C₃,C₄, and C₅)respectively. As evidenced from calculated and observed mass loss, where the first stage of mass-loss to confirm the existing of water hydration in some complexes and solvent molecules in the ligand and its complexes. The final stage of mass-loss in the thermal decomposition of some complexes gave oxides or sulfide as final residue depending on the altimetry between the metal and binding atom of the ligand. This refers to the stability of these oxides or sulfides within the decimate temperatures range. The ligand and its complexes are stable at room temperature. The thermal analyses data of ligand and its complexes were listed in the Table (2). The Thermograph of the ligand (L) and its Co-complex (C₁) are shown in the Figures (1 and 2).

Results and Discussion

The element analysis data of the prepared (L) and its complexes with [Co(II), Ni(II), Cu(II), Zn(II), and Cd(II)] ions are in good convention with the calculated results from expected formula of each synthesized compounds as listed in table(1).

FTIR Spectra

The FTIR-spectra of synthesized ligand and its synthesized complexes were recorded in (KBr) and (CsI) disk. The IR spectrum of ligand (L) was shown a sharp absorption band at (1668.31 cm⁻¹) which attributed to stretching vibration of $\nu(\text{C}=\text{O})$ which was hifted to (1650.95, 1668.31 with shoulder, 1685.67, 1656.74.and 1668.31 broad cm⁻¹ in

Thermal Analysis of L and its Metal Complexes

The first stage of mass-lose is resulted in the temperature ranges (180-250),(160-260),(70-270),(160-335), (150-270), and (145-325)°C

the (C₁-C₅) respectively [7, 8]. The weak band appeared at (1244.00cm⁻¹) is assigned to vibration of ν_{asy} (C=S) which was shifted to (1232.43, 1234.36, 1236.29, 1236.29, and 1247.86) cm⁻¹ in the (C₁-C₅) respectively [9, 10]. The weak band was appeared at (742.54 cm⁻¹) was assigned to ν_{sy} (C=S) which was shifted to (765.69, 761.83, 757.97, 763.76, and 748.33) with sharp bands in C₃, C₅[11,12]. The sharp and strong band appeared at (1145.64cm⁻¹) which is attributed to vibration of ν (C-N) of the ligand which was shifted to (1149.50, 1153.35, 1147.57 and 1153.35 cm⁻¹) these weak bands are attributed to ν (C-N) for C₁, C₃, C₄ and C₅, and split band at (1147.57, 1134.07cm⁻¹) in the C₂[13,14]. The weak band appeared at (3421.48cm⁻¹) is attributed to stretching vibration of ν (NH) which was shifted to (3421.00, 3284.55, 3421.48, 3438.84, 3377.12, and 3400.27) cm⁻¹ in the (C₁-C₅)[10, 15].

In the C₂, C₄ the peak appeared at (3477.42, 3377.12) cm⁻¹ was assigned to ν (H₂O)[16]. In the C₁ the peak was appeared at (640.00cm⁻¹) was assigned to coordinated water [17]. The absorption bands were appeared at (349.09-383.81cm⁻¹) are attributed to stretching vibration of ν (M-S) for (C₁-C₅) [18, 19]. The absorption bands were appeared at (592.11 - 609.46cm⁻¹) are attributed to stretching vibration of ν (M-O) for (C₁-C₅) [20, 16]. The IR spectra of ligand and its Co-complex (C₁) are shown in the Figures (3 and 4) and the data listed in the Table (3).

Molar Conductance

The molar conductances of all synthesized complexes of were measured in DMSO at room temperature. The values obtained lie in the range (1.9-58.0 S.cm².mol⁻¹), these indicate that all the synthesized complexes are non-electrolyte except C₁ was electrolyte. The data of molar conductance were listed in the Table (4).

Magnetic Susceptibility

According to the magnetic moment values, all the synthesized complexes are paramagnetic except complexes (C₄ and C₅) are diamagnetic because the zinc and cadmium ions have filled *d*-orbital. The data of magnetic susceptibilities were listed in the Table (4).

Electronic Spectra

The UV-Vis. Spectra of the ligand and its metal complexes were established in ethanol

at (10⁻⁴M) in the ligand and (10⁻³ and 10⁻⁴M) in the complexes at room temperature in the region (200-1100) nm. The ligand was showed two bands at (247,287) nm were assigned to ($\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$) transitions, which are shifted to [(236,267), (290, 319,332), (238, 279), (235, 269), and (237, 250)] nm in C₁-C₅ respectively [21, 22]. The bands were appeared at (394 nm in C₂, 316nm in C₃ and 412nm in C₅) were attributed to charge transfer (CT) (L→M), which C₁ was appeared three bands at (570, 612, 654) nm, C₂ appeared three bands at (826,856, 960) nm, and C₃ appeared band at(644)nm and these bands were attributed to d-d transitions[22 ,19 ,23]. There are no d-d transitions in C₄, and C₅ because of fill d-orbital in the Zn and Cd ions [24]. The electronic spectra of the ligand and its Co-complex (C₁) were shown in the figures (5 and 6) and their data were listed in the Table (4).

The NMR Spectra

¹H NMR Spectra

The ¹H NMR spectra for ligand and its (Ni (II)-L) (C₂) complexes were registered in DMSO as solvent. The free ligand was shown multiple peaks from δ (7.11-8.73ppm) refer to aromatic ring which are shifted to δ (6.95-8.55ppm) in the C₂ [25, 26]. The peak appeared at δ (11.76ppm) refer to the proton of (NH) for CONH in the ligand that was shifted to δ (11.58) ppm in the C₂ complex [5, 10]. The peak appearance of a signal at δ (12.70 ppm) attributed to refer to NH proton CSNH for ligand and shifted to δ (12.55ppm) in the C₂ [13, 7]. And the weak peak was appeared at δ (2.09 ppm and 1.91ppm) refer to CH₃ of ethanol in ligand and its Ni-complex, and CH₃ for acetate in the nickel. The single peak appear in δ (3.31-4.08 ppm) refer to protons of H₂O for DMSO in the ligand and its complex (moisture), and refer to water molecule in the complex. The peak were appeared at δ (2.47-2.89) refer to solvent [27, 17]. The ¹H NMR spectra and its spectral data of (L) its Ni-complex (C₂) are shown in the Figures (7 and 8) and listed in the Table (5).

¹³C NMR Spectra

In the free ligand, the aromatic ring appear in the δ (120.22-137.97ppm) which is shifted to δ (120.26 -137.87 ppm) in the nickel (C₂) [5]. The peak was appeared at δ (168.24ppm) was assigned to carbonyl group (C=O) in ligand which are shifted to δ (168.10ppm) in

the nickel (C₂) and refer to carbonyl group of acetate in the nickel (C₂) [10]. The thiocarbon C=S group appear in δ (179.13ppm) which are shifted to δ (178.71ppm) in the nickel(C₂) [10,13,5], and the two number refer to carbonyl group for acetate in the Nickel, and the peak appeared at δ (40.07-42.23ppm) was corresponded to the solvent peak (DMSO)[28 80]. The ¹³CNMR spectra for (L) and its Ni-complex (C₂) were shown in the Figs. (9 and 10) and listed in the Table (6). According to the spectral data and measurements mentioned above of the synthesized complexes, the suggested structures of these complexes (C₁,C₂,C₄ and C₅) were concluded as octahedral geometry except copper-complex(C₃) was appeared as a distorted octahedral as shown in Figures(11-15).

In vitro Antibacterial Activity

The antibacterial activities of ligand and its metal complex were screened against test bacteria (*Staphylococcus aureus* and *Bacillus*) (gram positive+) and (*Escherichia*) (gram negative-). Agar, (well-diffusion method) used to determine the activity [30, 31]. The concentration of the ligand and its complexes are (10⁻², 10⁻³, 10⁻⁴) M using DMSO (dimethylsulphoxide) as a (solvent). Ampicillin (antibiotic) was used as standard. The inhibition zones of the complexes were measured in (mm). The antibacterial activity in-vitro was investigated for the synthesized complexes (L1,C1-C5) at concentration (10⁻²-10⁻⁴)M against growth of (*Staphylococcus* and *Bacillus*) as gram positive and (*Escherichia Coli*) as gram negative.

The most synthesized complexes were effective against (*Bacillus*) as gram positive only. The antibiotic (Ampicillin) was showed good activity against as gram negative (*Escherichia Coli*) and showed no activity against gram positive (*Staphylococcus aureus* and *Bacillus*). Many factors were reported to control the biological activities of metal complexes: Type of ligand, type of metal, charge of complex, the transition series, and configuration of metal ion and geometry of metal complex [32].

The antibacterial data of ligand and its metal complexes were showed in the Figs. (16 and 17) and the data were listed in the Table (7). Corrosion Inhibitors. A corrosion inhibitor is a chemical substance which, when added in small concentrations to an environment, minimizes or prevents corrosion. Corrosion

inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, required, for example, to prevent corrosion that may result from accumulation of small amounts of an aggressive phase [33]. Corrosion can be controlled by removing the corrosive species in the medium. Inhibitors that decrease corrosively of the medium by scavenging the aggressive substances are called environmental conditioners or scavengers [34]. The presence of L1 and three complexes causes a prominent decrease in the corrosion rate i.e. shift both anodic and cathodic curves to lower values of current densities. Values of corrosion current densities (i_{corr}), corrosion potential (E_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c), inhibition efficiency (IE %), weight loss (w. L) and penetration losses (P.L) are listed in Table (8).

IE% can be calculated by مصدر

$IE\% = [w^0 - w/w^0] * 100 \dots (1)$, $IE\% = [I_{corr}^0 - I_{corr} / I_{corr}^0] * 100 \dots (2)$ where w^0 , w are weight loss for C.S in blank and inhibited soln. and I_{corr}^0 are the corrosion current densities for C.S in blank and inhibited soln., it is clear that i_{corr} decreased after adding L and the three complexes and L-Cd lead to the highest corrosion inhibition 82.5%. There is some shifted to more positive value of E_{corr} with L1, Ni-L and Cd-L1, while Cu-L1 shifted E_{corr} to more negative E_{corr} value. Corrosion potential indicates to thermodynamic feasibility according to the following eq. $\Delta G = -n f E_{corr} \dots (3)$

Where (which considered being equal to 2) is the number of electron involved in the anodic process. It is mean that L1 and Ni-L1, Cd-L1 cause to decrease the feasibility of metal to corrodes, while Cu-L1 lead to increase ΔG value and then increase the feasibility of metal corrosion. All ΔG value is listed in the Table (8). According to the P.L represented in table (8), L1 and Ni-L1 lead to decrease P.L, while Cu-L1 and Cd-L1 lead to increase P.L; that means adding inhibitors cause to a change in the type of corrosion between general corrosion to localized corrosion (pitting corrosion) by increasing P.L.

The corrosion inhibitor data of ligand and its metal (Ni, Cu and Cd) complexes were showed in the Figs. (18) And the data were listed in the Table (8).

Table1: Physical properties and analytical data of ligand and its metal complexes

Sym.	Color	Decom. Temp. (m.p.)°C	Yield %	% Element Analysis Found (Cal.)				% Metal Found(Cal.)
				%C	%H	%N	%S	
L	white	136-138	67	68.58 (68.19)	4.95 (5.68)	8.42 (7.95)	9.17 (9.09)	-
C ₁	blue	110	58	59.62 (59.28)	4.52 (4.69)	7.03 (6.75)	7.63 (7.71)	6.43 (7.07)
C ₂	Light green	100	56	60.06 (59.94)	5.58 (4.63)	7.52 (6.82)	7.04 (7.79)	6.34 (7.15)
C ₃	green	162	62	60.96 (60.26)	4.11 (4.53)	7.48 (6.86)	8.63 (7.84)	8.00 (7.77)
C ₄	Off white	100	64	60.23 (59.47)	4.78 (4.59)	6.13 (6.76)	6.12 (7.73)	7.35 (7.89)
C ₅	white	180	61	57.31 (56.85)	3.95 (4.28)	7.13 (6.47)	8.87 (7.39)	13.74 (12.98)

Table 2: The thermal analysis data (TG and DTG) of ligand and its metals complexes

Comp.	Step	Temp. range of decomposition at TG °C	Peak temp. at DTG °C	Suggested formula of loses	% Mass loss	
					Found	Cal.
L	1	180-250	221.2	EtOH, C ₅ H ₅	30.72	31.53
	2	250-415	325.7	C ₁₀ H ₇ , CNCNC	54.00	54.26
	3	415-595	465.1	O, H ₂	5.69	5.11
	4	>595	-	S	9.57	9.09
C ₁	1	160-260	220	0.5EtOH, C ₁₀ H ₇ , CH ₃ COO	24.71	25.18
	2	260-378	300	C ₁₀ H ₇ , 2C ₆ H ₅ NH	36.97	37.47
	3	378-592	470	CH ₃ COO, H ₂ O, 2CONHC	22.88	22.53
	4	>592	-	S, CoS	15.44	14.80
C ₂	1	70-180	120	0.5EtOH, 0.5H ₂ O, C ₄ H ₄	10.70	10.23
	2	180-330	260	CHCNH, C ₁₀ H ₇ , C ₆ H ₅ NH,	30.63	31.55
	3	330-595	450	C ₁₀ H ₇ C	16.93	16.93
	4	>595	-	CSNH, CONHCS, 2CH ₃ COO, NiO	41.74	41.26
C ₃	1	160-335	230	0.5EtOH, 2C ₁₀ H ₇ C, 2C ₆ H ₅ NH	58.79	59.39
	2	335- 595	452	CH ₃ COO, O ₂ , CSNH, NH	20.73	20.20
	3	>595	-	CH ₃ COO, C, CuS	20.46	20.39
C ₄	1	150-270	215	0.5EtOH, 0.5H ₂ O, C ₁₀ H ₇ CO, C ₁₀ H ₇	38.23	37.95
	2	270-355	312	C ₆ H ₅ NHCSNH, CO, C ₆ H ₅	30.97	30.94
	3	355-595	460	NHCNH, CH ₃ COO	12.92	12.20
	4	>592	-	CH ₃ COO, ZnS	17.87	18.89
C ₅	1	145-345	298.9	0.5 EtOH, 2C ₆ H ₅ NH, C ₁₀ H ₇ , C ₁₀ H ₇ CO, 2CH ₃ COO	70.65	70.14
	2	345-595	380	CSNH, CSNHC	14.97	15.02
	3	>595	-	CdO	14.38	14.83

Table 3: Infrared spectral data in (cm⁻¹) of ligand and its complexes

Comp.	ν C=O	ν C-N	ν C=Ss	ν C=Sas	ν NH	ν M-O	ν M-S
L	1668.31	1145.64	742.54	1244.00	3421	-	-
C ₁	1650.95 shold.	1149.50br.	765.69	1232.43	3284.55	599.82	368.38
C ₂	1668.31 br.	1147.57	761.83	1234.36	3421.48	609.46	383.81
C ₃	1685.67	1153.35	757.97	1236.29	3438.84	597.89	370.31
C ₄	1656.74	1147.57 br.	763.76	1236.29	3377.12	609.46	349.09
C ₅	1668.31	1153.35	748.33	1247.86	3400.27	592.11	349.09

Table4: The electronic spectral data and conductivity measurement of ligand and its complexes

Comp	Wave length λ (nm)	Wave no. $\bar{\nu}$ (cm ⁻¹)	Assignment	Molar. cond. ($\text{S cm}^2 \text{mol}^{-1}$)	μ_{eff} (B.M)	Suggested Geometry
L	247	40486	$\pi \rightarrow \pi^*$	-	-	-
	287	34843	$n \rightarrow \pi^*$			
C ₁	236	42373	$\pi \rightarrow \pi^*$	58	5.9	Octahedral
	267	37453	$n \rightarrow \pi^*$			
	570	17543	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$			
	612	16339	${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$			

	654	15290	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$			
C ₂	290	34482	$\pi \rightarrow \pi^*$	3.8	3.5	Octahedral
	319	31347	$n \rightarrow \pi^*$			
	332	30120	$\pi \rightarrow \pi^*$			
	394	25380	C.T.(L→M)			
	826	12106	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$			
	856	11682	${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$			
	960	10417	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$			
C ₃	238	42017	$\pi \rightarrow \pi^*$	20.5	1.7	Distorted Octahedral
	279	35842	$n \rightarrow \pi^*$			
	316	31645	C.T. (M →L)			
	644	15527	${}^2E_g \rightarrow {}^2T_{2g}$			
C ₄	235	42553	$\pi \rightarrow \pi^*$	1.9	diamagnetic	Octahedral
	269	37174	C.T and $n \rightarrow \pi^*$			
C ₅	237	42194	$\pi \rightarrow \pi^*$	4.0	diamagnetic	Octahedral
	250	40000	$n \rightarrow \pi^*$			
	412	24272	C.T. (M →L)			

Table 5: The ¹HNMR spectral data of ligand and its complexes

Assignments	L	Ni(L) ₂
Ar-H	δ(7.11- 8.73)	δ (7.11- 8.73)
CONH	δ(11.76)	δ(11.58)
CSNH	δ (12.70)	δ(12.55)

Table 6: The ¹³CNMR spectral data of ligand and its complexes

Assignments	L2	Ni(L) ₂
Ar-C	δ(120.22-137.97)	δ(120.26 -137.87)
C=O	δ(168.24)	δ(168.10)
C=S	δ(179.13)	δ(178.71)

Table 7: The antibacterial data of ligand and its metal complexes

Comp.	Inhibition zone Escherichia coli (-)			Inhibition zone Bacillus (+)			Inhibition zone Staphylococcus aureus (+)		
	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻²	10 ⁻³	10 ⁻⁴	10 ⁻²	10 ⁻³	10 ⁻⁴
L	-	-	-	16	18	19	-	-	-
Co(L) ₂	5	-	-	15	6	6	-	-	-
Ni(L) ₂	4	1	-	14	6	13	2	1	2
Cu(L) ₂	1	-	-	23	-	-	-	-	-
Zn(L) ₂	4	-	-	19	16	17	-	-	-
Cd(L) ₂	-	-	-	8	21	24	-	-	-
Ampicillin	17	13	12	-	-	-	-	-	-

Table 8: Corrosion kinetic parameter for C.S with different inhibition complexes in 3.5%NaCl at 25C temperature

	OCP/ mV	E _{corr} / mV	i _{corr} /μA. cm ⁻²	bc/mV .dec ⁻¹	ba/mV .dec ⁻¹	w.l/g.m ² .d ⁻¹	P.L/mm. y ⁻¹	IE%	R _p / Ω.cm ²
Blank	-562	-628.3	306.83	-209.3	74.9	2.47	3.34	0	78.06
Ligand	-523	-553.1	139.79	-140.6	120.2	1.13	1.52	54.4	201.28
Ni	-549	-605.6	120.96	-160.9	118.7	9.73	1.32	60.5	245.2
Cu	-566	-570	60.36	-67.1	78.5	4.86	6.57	80.3	260.2
Cd	-543	-532.2	53.68	-94.9	95.4	4.32	5.84	82.5	384.8

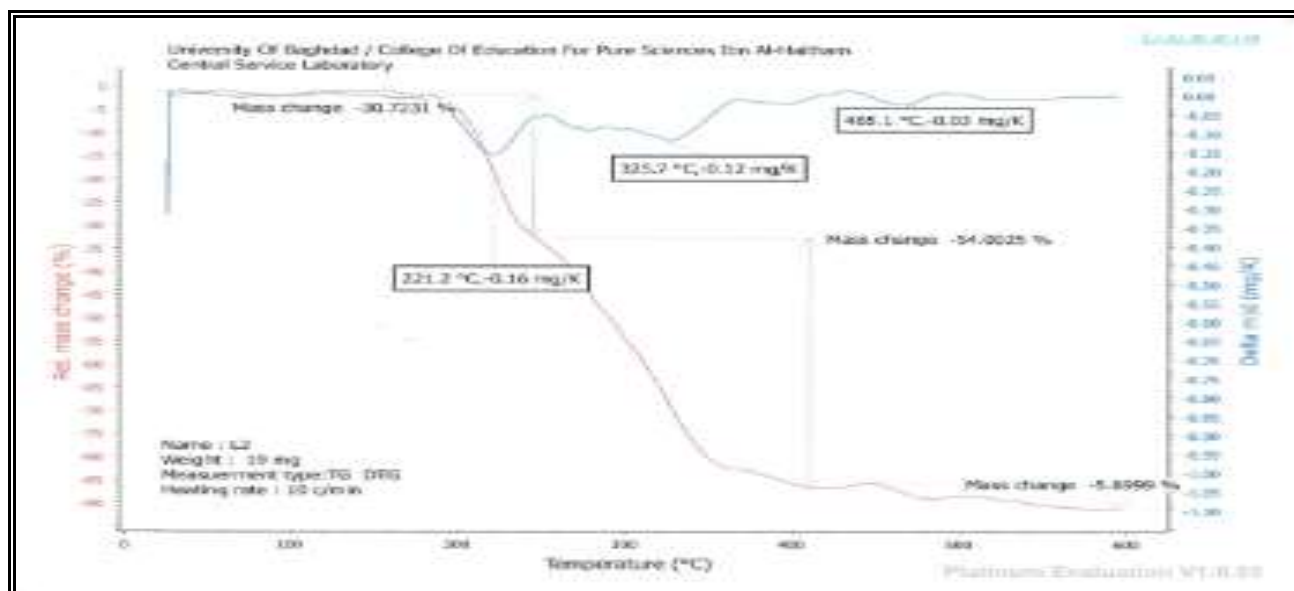


Fig.1: Thermograph of L

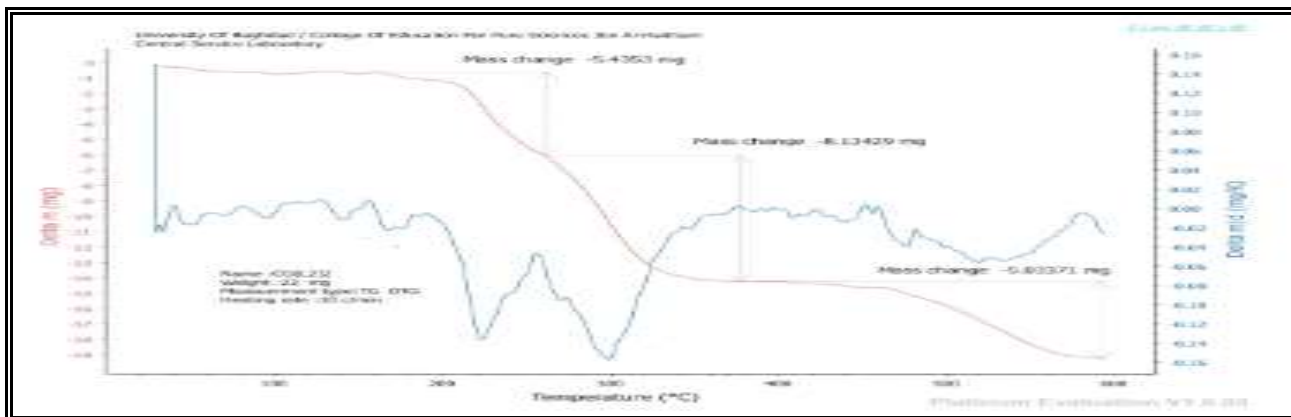


Fig. 2: Thermograph of C1

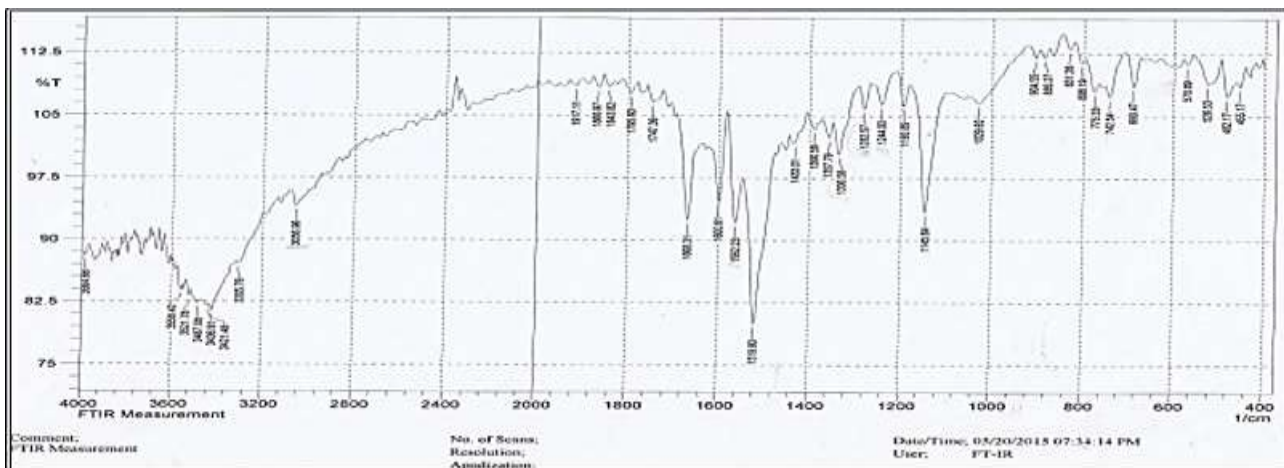


Fig. 3: the FTIR spectrum of L

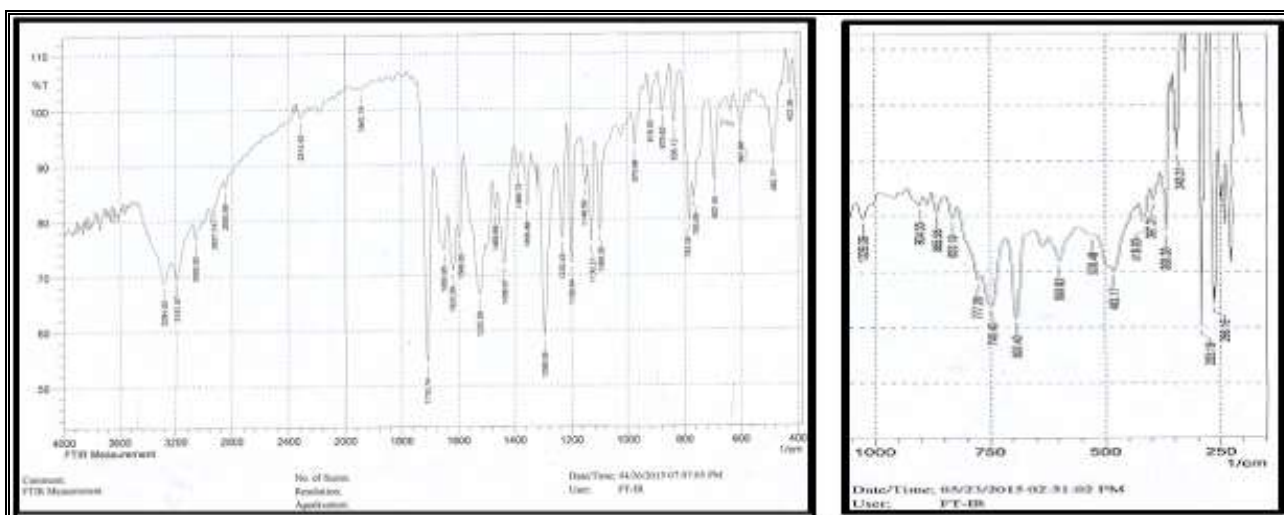


Fig.4: the FTIR spectrum of C1

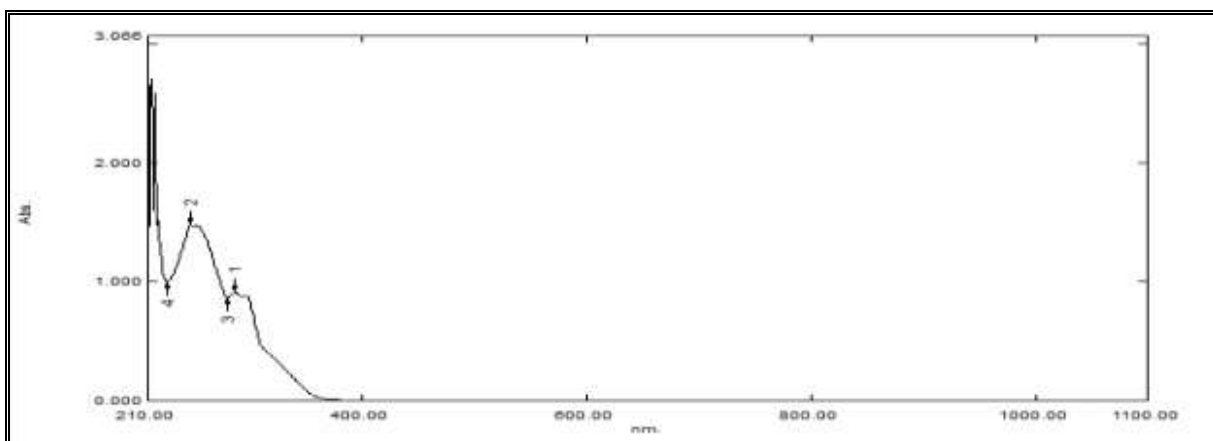


Fig.5: the electronic spectrum for L

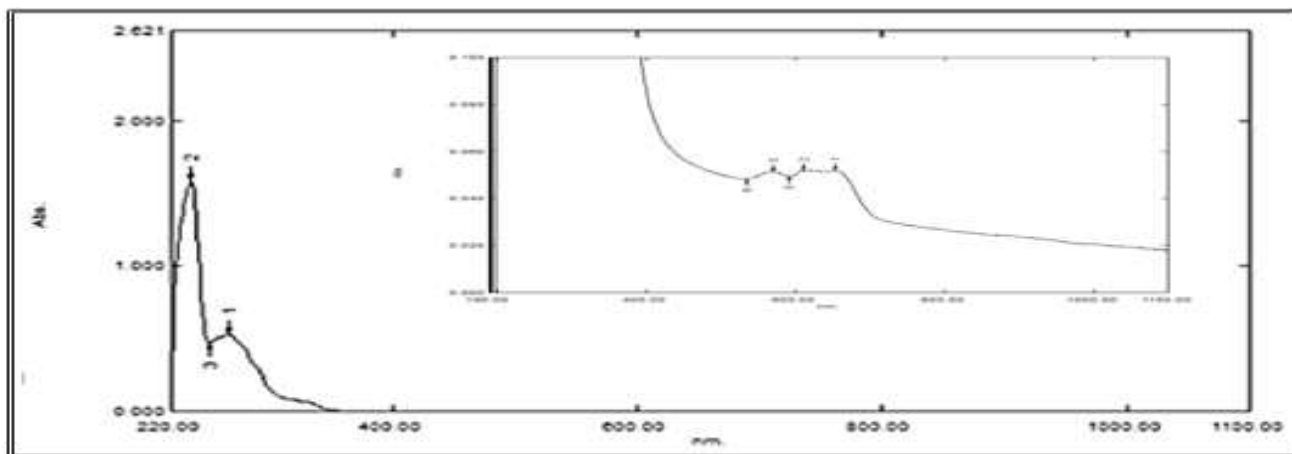


Fig. 6: the electronic spectrum for C₁

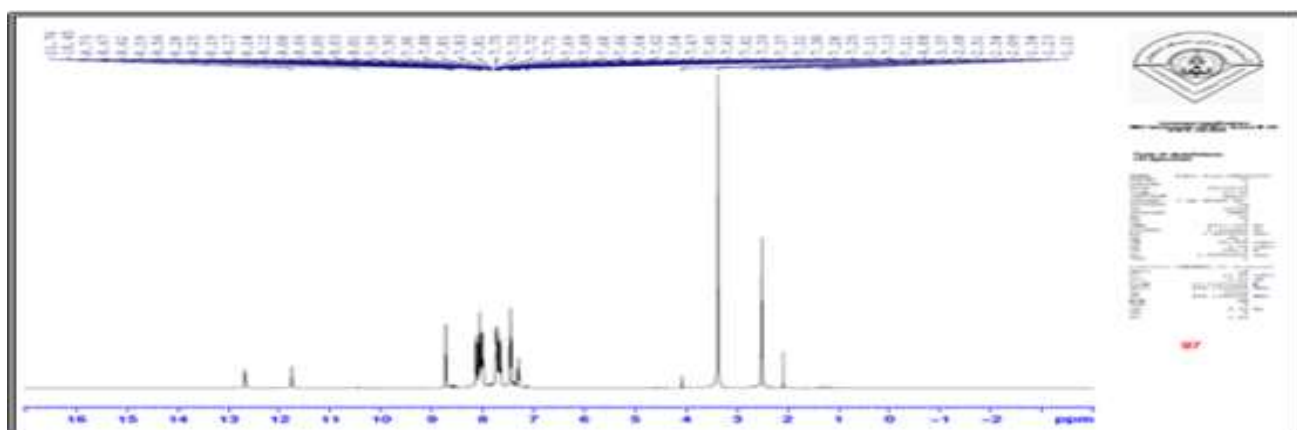


Fig. 7: the ¹H NMR spectrum of L

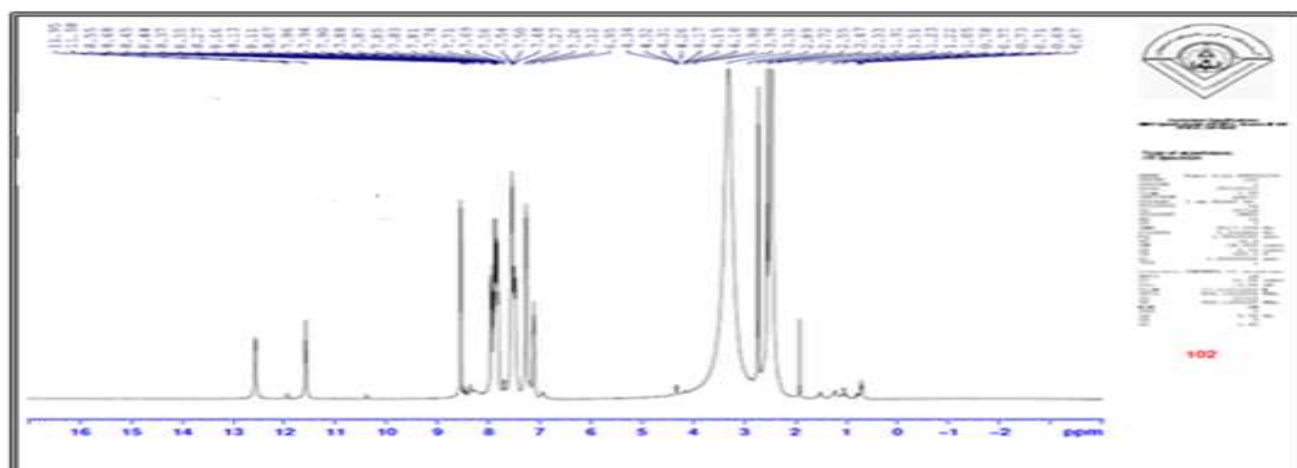


Fig. 8: the ¹H NMR spectrum of C₂

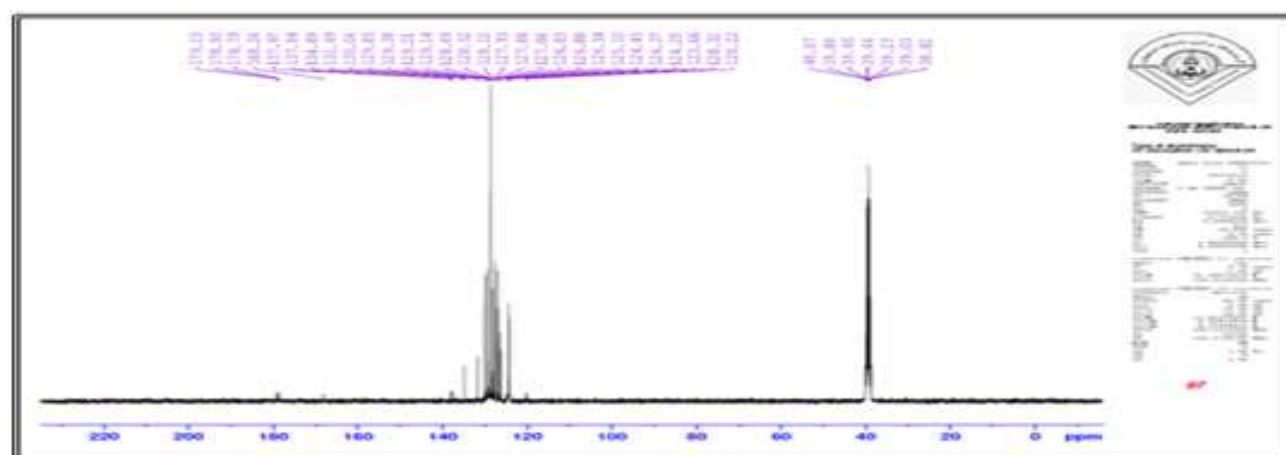


Fig. 9: the ¹³C NMR spectrum of L

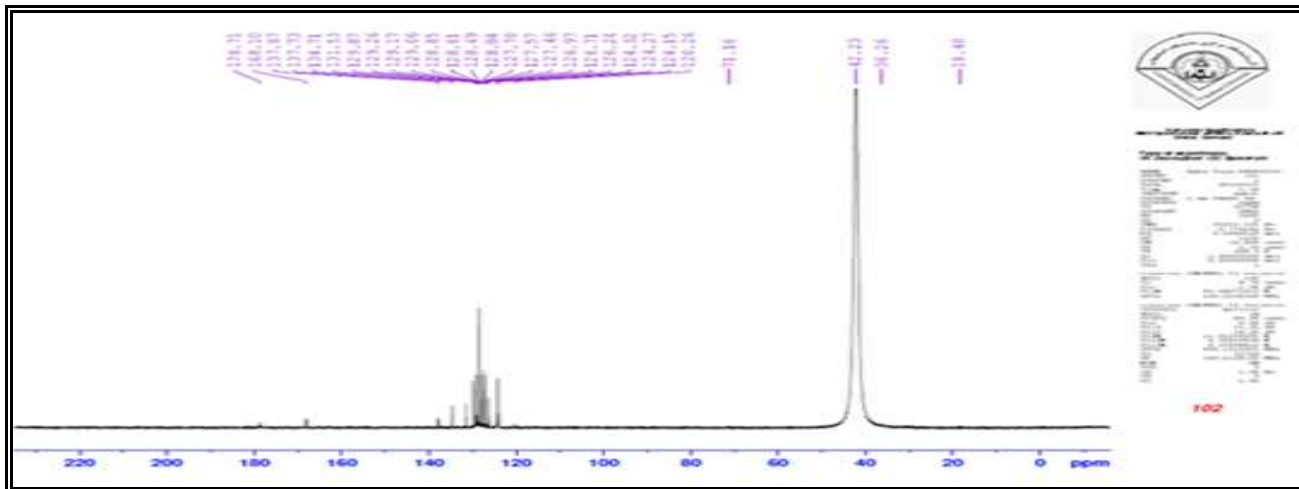


Fig .10: the ¹³C NMR spectrum of C₂

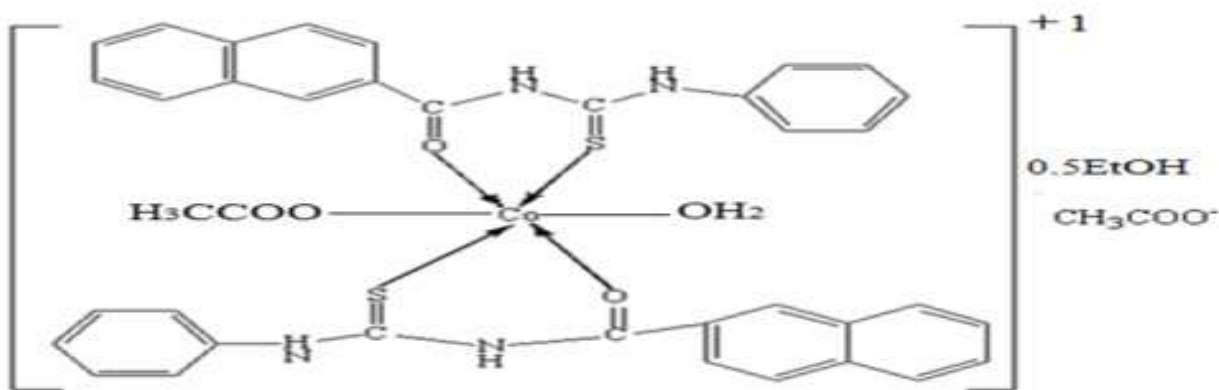


Fig.11: The structure of [Co (L) 2(OOCCH3) (OH₂)] (OOCCH₃) (0.5EtOH)

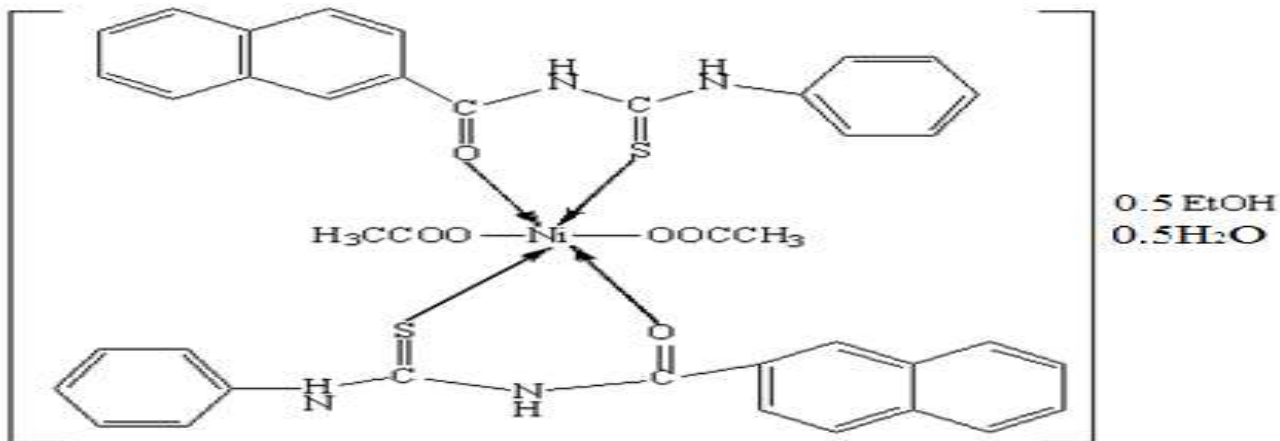


Fig. 12: The structure of [Ni (L) 2(OOCCH₃)] (0.5EtOH) (0.5H₂O)

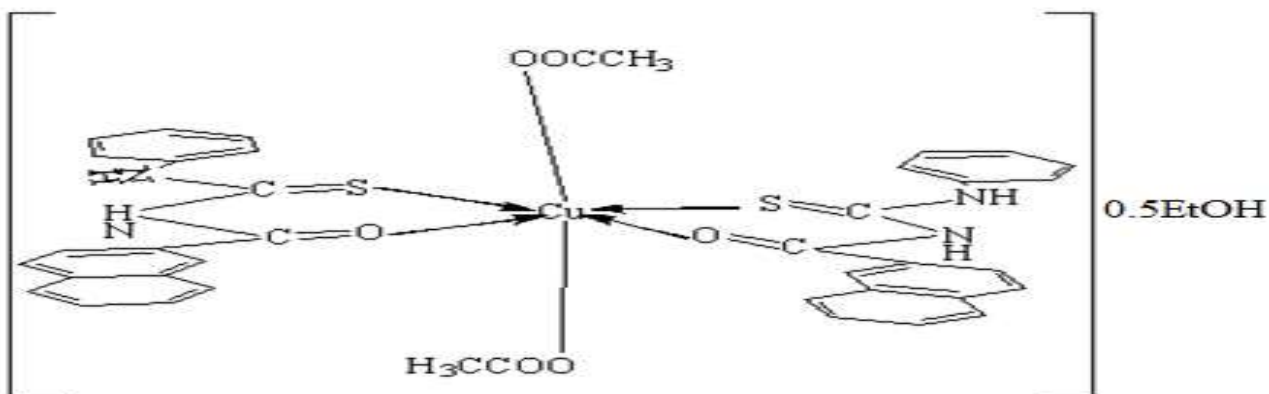


Fig. 13: The structure of [Cu (L) 2(OOCCH₃)] (0.5EtOH)

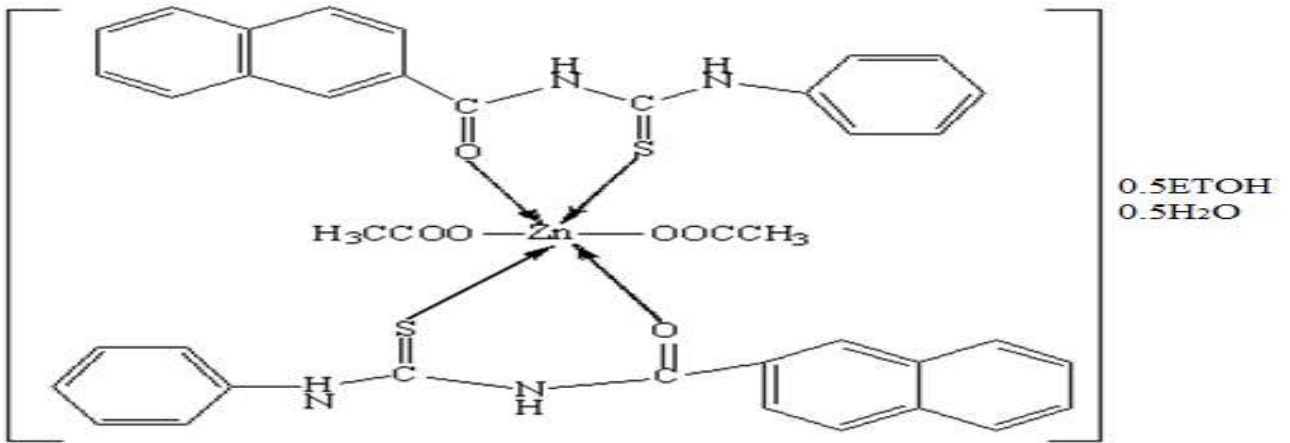


Fig.14: The structure of [Zn (L) 2(OOCCH3)] (0.5EtOH) (0.5H2O)

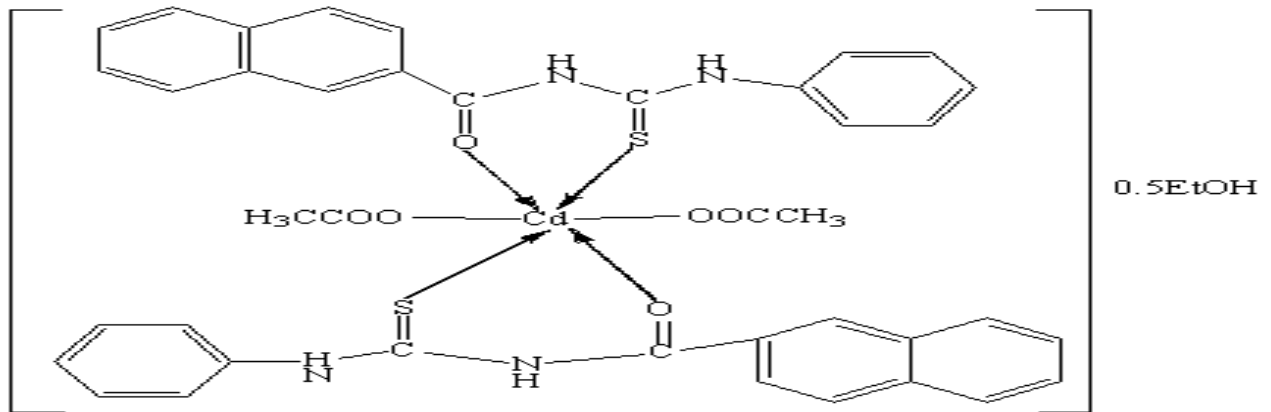


Fig. 15: The structure [Cd(L)2(OOCCH3)2] (EtOH)

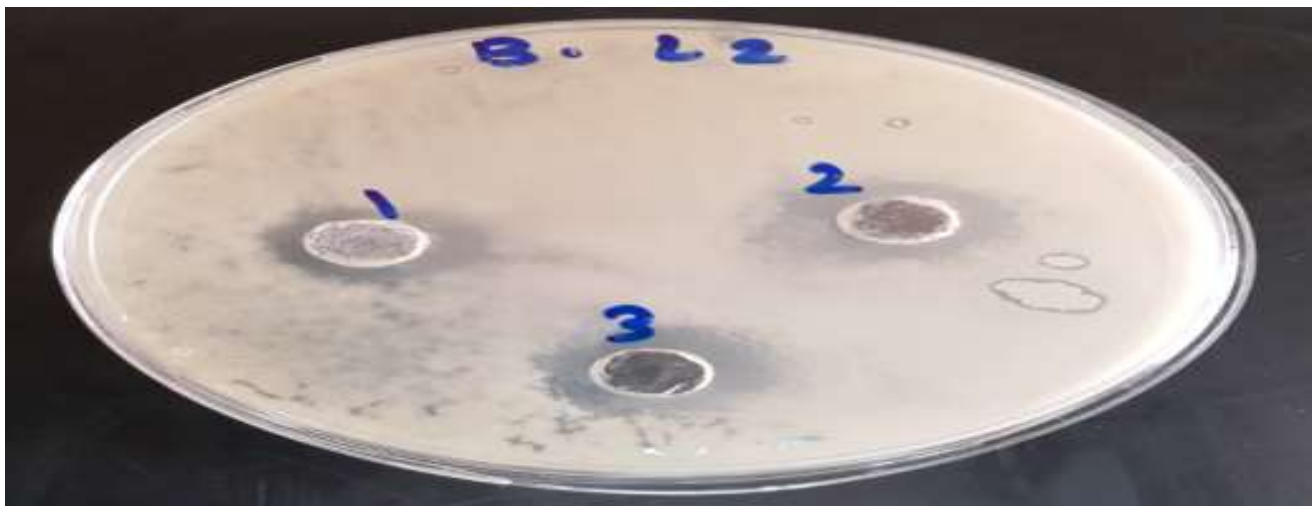


Fig. 16: Inhibition zone of L against of positive gram bacteria (Bacillus)

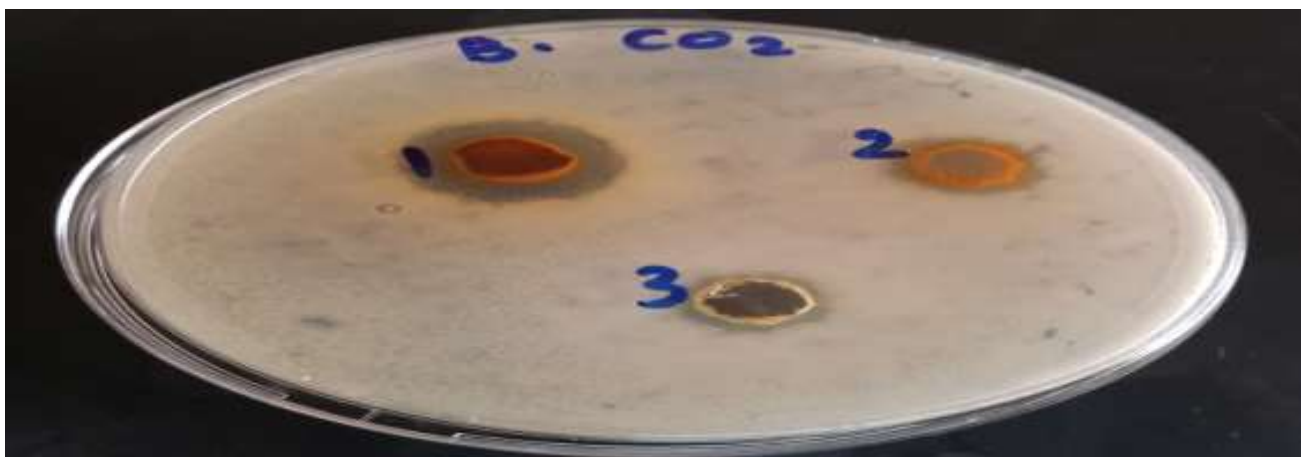


Fig.17: Inhibition zone of Co (L) 2 against of positive gram bacteria (Bacillus)

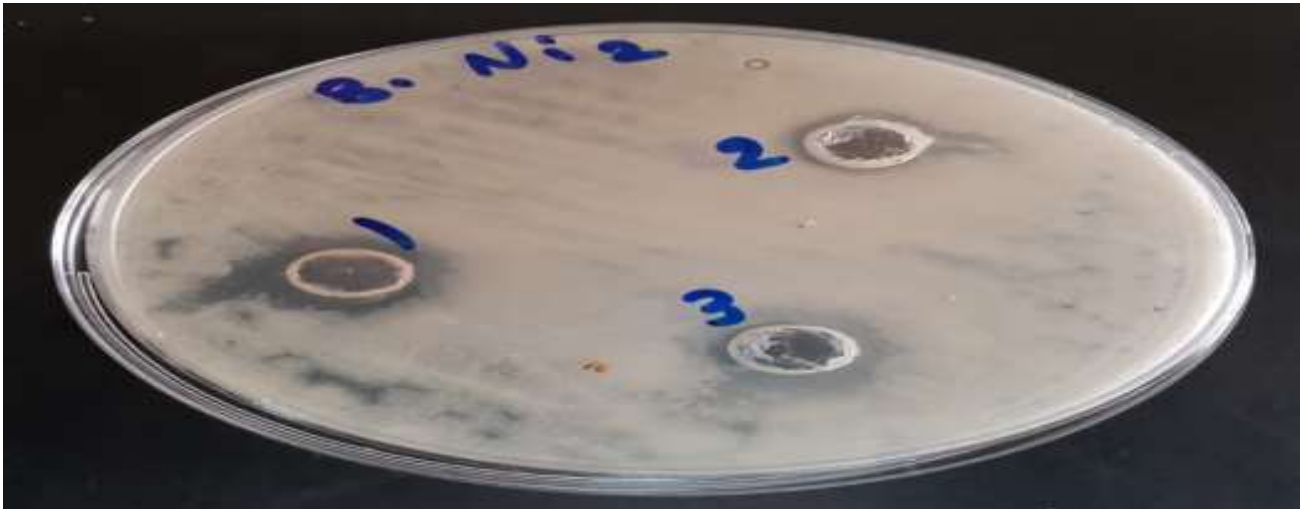


Fig. 18: Inhibition zone of Ni (L) 2 against of positive gram bacteria (Bacillus)

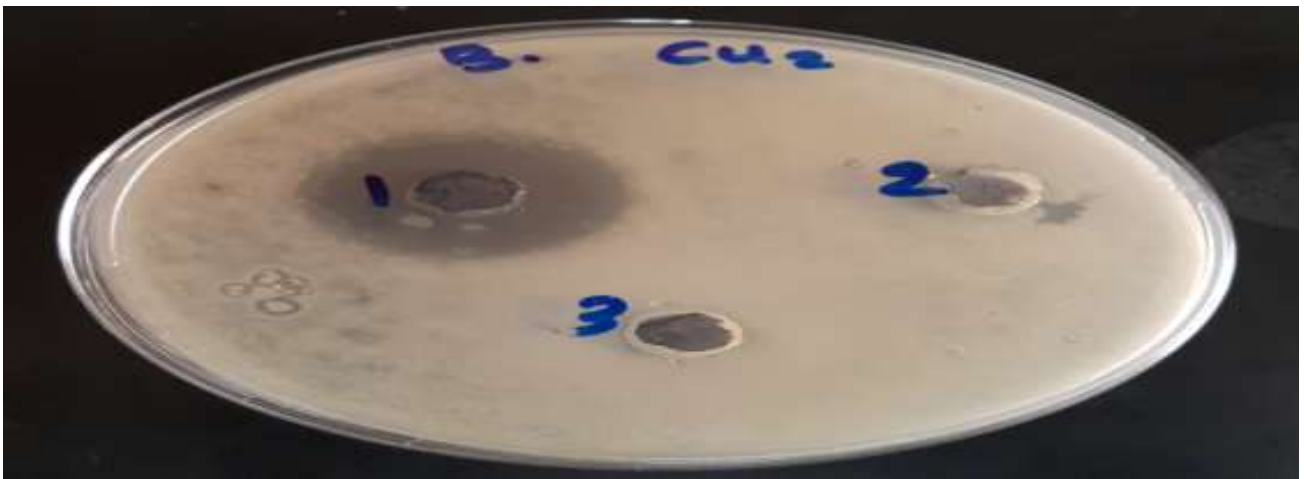


Fig. 19: Inhibition zone of Cu (L) 2 against of positive gram bacteria (Bacillus)

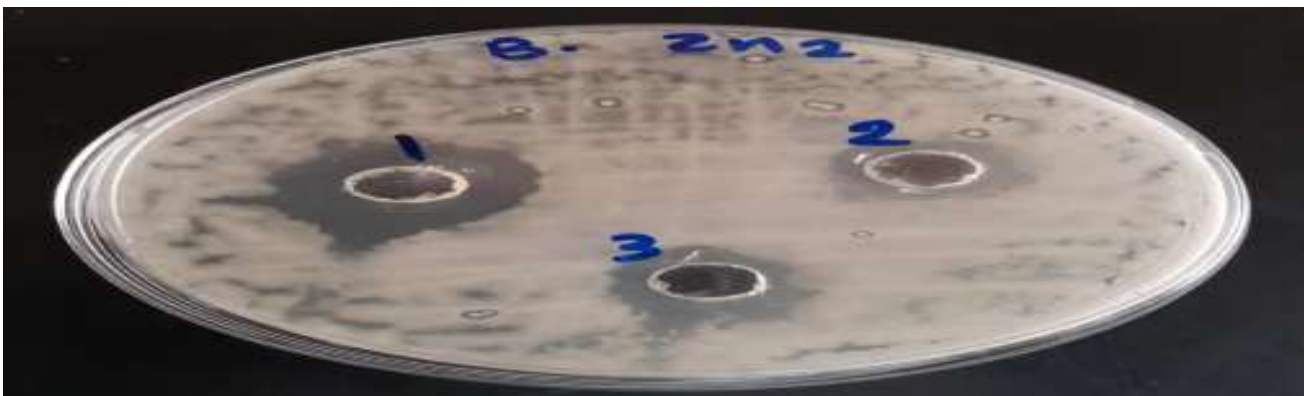


Fig. 20: Inhibition zone of Zn (L) 2 against of positive gram bacteria (Bacillus)

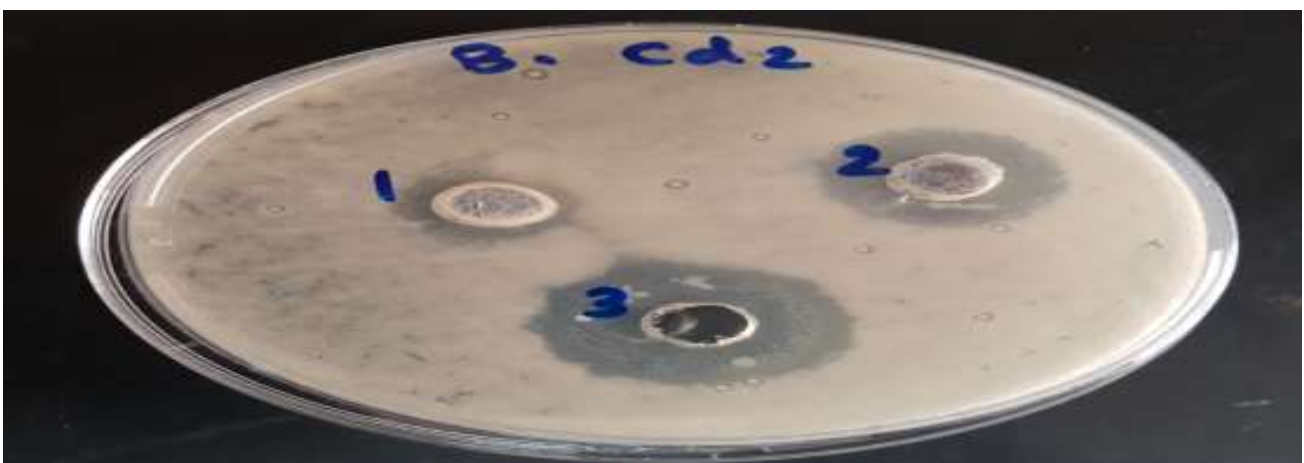


Fig. 17: Inhibition zone of Cd (L) 2 against of positive gram bacteria (Bacillus)

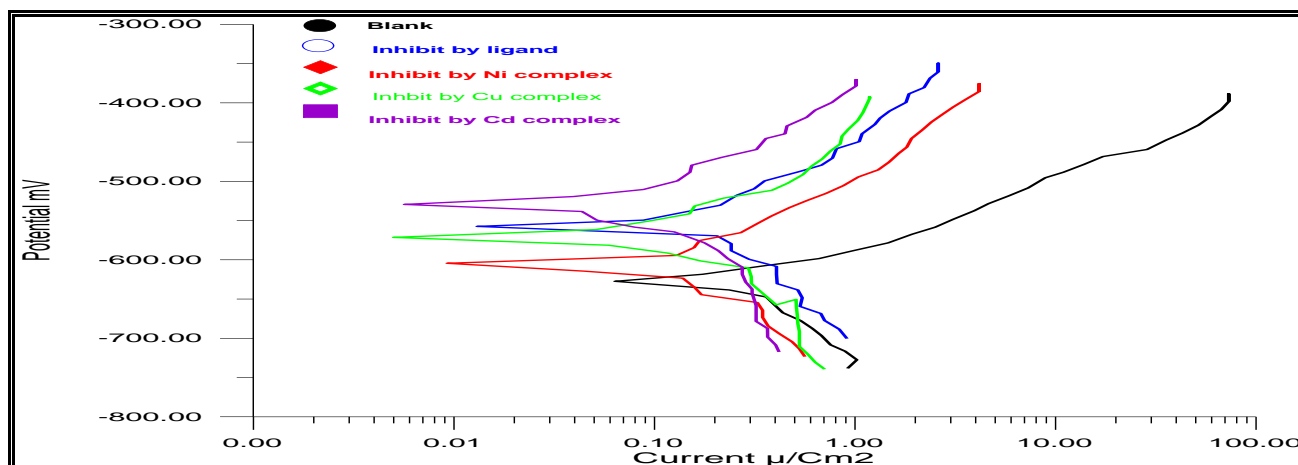


Fig. 18: The polarization curves of blank, ligand, Ni, Cu, Cd complexes using carbon steel at 25 temperatures

Conclusion

The thiourea (L) was found to be linked with [Co (II), Ni (II), Cu (II), Zn (II), and Cd (II)] ions through sulfur atom of thiocarbonyl, and oxygen atom of carbonyl group. The chemical structure for the ligand and its complexes have been studied by different physiochemical technique FTIR, NMR, UV-

Vis spectroscopies, thermal analysis ,atomic absorption, conductivity measurements, magnetic Susceptibilities and element analysis were gave a results corresponding to mole ratio of (2:1) and the structures of the synthesized complexes were octahedral geometry expect the Cu-complex was distorted octahedral geometry.

References

1. Abdul fattah MA, Zaineb IL, Ahmed EZ (2014) "Synthesis and use of thiourea derivative (1-phenyl-3-benzoyl-2-thiourea) for extraction of cadmium ion", International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering, 8: 118-120.
2. Tarjeet S, Ram L, Girija SS (2013) "Chemo selective N-benzoylation of aminophenols employing benzoylthiocyanates", Arabian Journal of Chemistry, 1-4.
3. Gun B, Bülent Z, Esmâ K, Nevzat K, Hakan A (2012) "Determination of the ionization constants of some benzoyl thiourea derivatives in dioxane-water mixture", Journal of Chemistry, 2013: 1-7.
4. Omer AH, Ali MO, Abeer A (2008) "Photodegradation Study of PVC By New Metal Complexes of Thiourea Derivatives", National Journal of Chemistry, 31: 501-513.
5. George MN, Constantin D, Mariana CC, Alexandru VM (2009) "Synthesis of isomeric N-(1-methyl-1-hpyrazole-4-carbonyl)-N'-(XYLYL)- thiourea and their antimicrobial evaluation", Farmacia, 57(5): 527-533
6. Bayazeed HA, Yousif MS (2010) "Synthesis, characterization and biological activity of N-phenylN'-(2-phenolyl) thiourea (PPTH) and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), Pt(II) and Hg(II)", Oriental Journal of Chemistry, 26(3):763-773.
7. Aamer S, Naeem A, Hummera R, Sadaf R, Hameed A (2009) "Synthesis Characterization and Antibacterial Activity of Some 1-Aroyl-3-Aryl Thioureas", Chemistry, 18: 152-158.
8. Jian W, Qing S, Zhuo C, Ming H, Linhong J, Deyu H (2012) "Synthesis and Bioactivity of Pyrazole Acyl Thiourea Derivatives", Molecules, 17: 5139-5150.
9. Umasankar K, Chawada B, Boyapati S, Alavala RR (2014) "Synthesis Antimicrobial and Anticancer Activity of 1-[(aryllalkylidene) amino]-3-(4H--1, 2, 4-triazol-4-yl)thiourea", Journal of Pharmaceutical Chemistry, 1(1): 5-9.
10. Sohail S, Naghmana R, Muhammad A, Rizwan H, Peter J (2010) "Synthesis, spectroscopic characterization, crystal structure and pharmacological properties of some novel thiophene-thiourea core derivatives", European Journal of Chemistry, 1 (3): 221-227.

11. Rai BK, Rachana K (2013) "Synthesis, structural, spectroscopic and antibacterial studies of schiff base ligands and their metal complexes containing nitrogen and sulphur donor atom", *Orient. J. Chem.*, 29(3):1163-1167.
12. Rizwana B, Santha L S (2012) "Synthesis, Characterization and Antimicrobial Studies of Zn(II), Ni(II) and Cu(II) Complexes of a Schiff base derived from o-Vanillin and N-Allyl Thiourea", *Int. J. Chem. Tech. Res.*, 4(1): 464-473.
13. Mohammad B, Nasir I (2012) "Green synthesis of N-substituted-N'-aryl carbonyl bifunctional thioureas under solvent-free conditions", *Iranian Journal of Organic Chemistry*, 4: 837-840.
14. Abdullah MA, Khadija OB (2007) "synthesis of some new anils: part 1. Reaction of 2-hydroxy-benzaldehyde and 2-hydroxynaphthaldehyde with 2-aminopyridine and 2-aminopyrazine", *Molecules*, 12: 1796-1804.
15. Revathi V, Rajendran V (2013) "Growth and characterization of semi-organic nickel bis thiourea nitrate single crystal", *Der Pharma Chemica.*, 5 (4): 105-111.
16. Suraj BA, Deshpande MN, Deshmukh JH (2012) "Synthesis and Characterization Of Transition Metal Complexes Of Schiff Base Derived From Isatin And 2-Amino, 4-Chloro Benzoic Acid", *Rasayan. J. Chem.*, 5: 10-15.
17. Reda AAA, Abdel-Nasser MAA (2013) "Synthesis, Spectroscopic Characterization and Potentiometric Studies of a Tetradentate [N₂O₂] Schiff Base, N, N'-bis(2-hydroxybenzylidene)-1,1-diaminoethane and its Co(II), Ni(II), Cu(II) and Zn(II) Complexes", *Int. J. Electrochem. Sci.*, 8: 8686-8699.
18. Bayazeed HA, Yousif MS (2010) "Synthesis, characterization and biological activity of N-phenyl-N-(2-phenolyl) thiourea (PPTH) and its metal complexes of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Pd(II), Pt(II) and Hg(II)", *Oriental Journal of Chemistry*, 26(3): 763-773.
19. Shakru R, Subhashini NJP, Sathish KK, Shivraj (2010) "Synthesis, characterization and antimicrobial studies on Cobalt (II), Nickel (II), Copper (II) and Zinc (II) complexes of N, O, S donor Schiff bases", *J. Chem. Pharm. Res.*, 2(1): 38-46.
20. Hegazy WH, Gaafar AE-D M (2012) "Synthesis, characterization and antibacterial activities of new pd(II) and pt(IV) complexes of some unsymmetrical tetradentate Schiff bases", *American Chemical Science Journal*, 2(3): 86-99.
21. Iftikhar HB (2002) "Preparation, Characterization and biological evaluation of Schiff base metal complexes of some drug substances", Thesis, 185.
22. Sreesha SI (2008) "Transition metal complexes of Schiff bases with azide and thiocyanate as collgands: spectral and structural investigations", Thesis, 1-262.
23. Gehad GM, Mohamed MO, Ahmed MH (2006) "Metal Complexes of Schiff Bases: Preparation, Characterization, and Biological Activity", *Turk. J. Chem.*, (30), 361-382.
24. Pragathi MPJ, Anupama B, Gyanakumari C (2012) "Synthesis, spectral characterization, molecular modeling, and antimicrobial studies of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) complexes of ONO schiff base", *E-Journal of Chemistry*, 9(4): 2145-2154.
25. Robina A, Garima M, Manju LU, Tripti G (2013) "Triorganotin (IV) Complexes of Schiff Base Derived from Glycine: Synthesis, Characteristic Spectral Studies and Antifungal Activity", *Chem. Sci. Trans.*, 2(2): 389-394.
26. Gomathi V, Selvameena R, Subbalakshmi R, Valarmathy G (2013) "Synthesis, Spectral Characterization and Antimicrobial Screening of Mn(II), and Zn(II) Complexes Derived from (E)-1-1((p-tolylimino)methyl) naphthalene-2-Ol", *Orient. J. Chem.*, 29: 533-538.
27. Surya GKP, Tisa ET, Inessa B, Arjun P (2008) "Efficient green synthesis of α-aminonitriles, precursors of α-amino acids", *Royal Society of Chemistry*, 10: 1105-1110.
28. Alejandro B, Carmen N, Jose MS (2007) "Solvent free synthesis of racemic α-aminonitriles", *Synthesis*, 8: 1230-1234.

29. Ahmad, Beg A Z (2001) "Antimicrobial and phytochemical studies on 45 Indian medicinal plants against multi-drug resistant human pathogens, Journal of Ethno pharmacology, 74(2): 113-123.
30. Taqui Khan B, Najmuddin K, Shamsuddin S, Annapoorna K, Bhatt J (1991) "Synthesis, antimicrobial, and antitumor activity of a series of palladium(II) mixed ligand complexes, Journal of Inorganic Biochemistry, 44(1): 55-63.
31. Shelke VA, SM Jadhav, Shankarwar1 SG, Munde AS, Chondhekar1 TK (2011)" Synthesis, Characterization, Antibacterial and Antifungal Studies of some transition and rare earth metal complexes of N-benzylidene-2-hydroxybenzohydrazine, Bull. Chem. Soc. Ethiop., 25(3): 381-391.
32. Huda Kassim Jabur, Mahasin Faisal Alias, Tamara abed Al- Azez Kareem, (2012)" Preparation, characterization and biological activity of some complexes of potassium 2-carbomethoxy amino-5-trithiocarbonate 1, 3, 4-thiadiazole", J. Baghdad for Sci., 9(3): 511- 520.
33. Riggs OL, Nathan CC (1973) Corrosion Inhibitors, NACE, Houston, TX, 11.
34. Noack MG, Mater P (1982) 21(3): 26.