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Determination Antioxidant Activity for Metal Ion Complexes and Theoretical Treatment.

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ABSTRACT

Metal ions complexes are synthesized with the general formula; [M $Cl_2(L)_1$] and [M $(L)_2$], where M(II) = Co, Ni and Cu are reported. The structures of the ligands and the metal complexes were characterized by elemental microanalyses (C.H.N), FT-IR spectroscopy and UV-VIS spectroscopy, ^{1}H-NMR were recorded for the ligands, magnetic moment, chloride containing and molar conductivity studies. The Schiff base (HL_1) behaves as mono dentate ligand through one nitrogen atom of azomethen group coordinate for all metal ions. The Schiff base (HL_2) behaves as bidentate ligand through one nitrogen atom of azomethen group and one oxygen atom of phenyl group coordinate for all metal ions. The antioxidant activities of the ligands and the metal complexes were examined using the DPPH radical scavenging method the compounds exhibited antioxidant properties of scavenging free radicals. Hyper Chem-8 program has been used to predict structural geometries of compounds in gas phase.

Keywords: Antioxidant Activity, Theoretical Treatment, Co (II), Ni(II), Cu(II) Complexes, DPPH

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INTRODUCTION

Molecules are inhibiting the oxidation processes and removing free radicals known as Antioxidants [1]. A most of Antioxidants are poly substituted phenolic compounds [2]. A method for measuring activity antioxidants is 1,1-Diphenyl-2-picrylhydrazyl (DPPH) is a stable organic radical compound and its oxidative essay [3] is based on the measurement of the scavenging capacity of antioxidants towards it. The odd electron of nitrogen atom in DPPH is reduced by receiving a hydrogen atom from antioxidants to the resultant hydrazine [4]. The most common assays are those involving chromogen compounds of radical nature, which in the presence of an antioxidant disappear. This reaction can be easily followed by common spectrophotometric detection [5]. The DPPH radical is long-lived organic nitrogen radical with a deep purple color [5]. These are the condensation products of primary amines with carbonyl compounds and were first reported by Hugo Schiff [6-9] when –OH functional group is close to the azomethine group The Schiff base ligands are considered to be good chelating agents [10]. In azomethine derivatives, the C=N linkage is essential for biological activity, several azomethines were reported to possess remarkable antibacterial, antifungal, anticancer and diuretic activities [11]. Schiff base compounds constitute an important class of ligands which have been studied in coordination chemistry. Schiff base complexes are also known for their significant biological activities such as in photosynthesis and transport of oxygen in mammalian and other respiratory systems [12]. Due to the great flexibility and diverse structural aspects of Schiff bases, a wide range of these compounds have been synthesized and their activities have been studied [13]. Schiff's base and its complexes.have Several model systems, including: bidentate, tridentate, tetradentate, multidentate [14].

EXPERIMENTAL

Materials and methods

All chemicals were purchased from commercial sources and were used without further purifications $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, CH_3OH , C_2H_5OH ,and HCL from B.D.H, 2-aminophenol, 4-aminophenol and 4-Dimethylamino benzaldehyde from Fluka, DMSO from SDFCL, Gallic acid from Riedel and DPPH from sigma Aldrich.

Elemental microanalyses (C.H.N.) were performed by using (Euro vector model EA 3000, single V.3.O single Series elemental microanalyses. Melting points were obtained on a Stuart SMP -10 capillary. Metals were determined using a Shimadzu (A. A) 620 G. atomic absorption Spectrophotometer. Magnetic moments were measured with a magnetic susceptibility balance (Sherwood balance magnetic susceptibility model MSB-MK). Chlorine was determined using potentiometer titration method on a 686-Titro processor-665 Dosimat-Metrohm Swiss. The IR spectra (KBr disc) were recorded on shimadzu,(8400S spectrophotometer in the range of 4000 to 400 cm^{-1}. ^{1}H-NMR spectra were recorded in DMSO with TMS as an internal standard spectra were acquired in DMSO-d_6 solution using Brucker 300 MHz spectrometer, UV-Visible spectra were recorded using (Shimadzu1800A) spectrophotometer. Conductivity measurements were made with DMSO solutions using a Jenway 4071 digital conductivity meter at room temperature Conductivity measurements were made with using a Philips PW- digital.

Preparation of Schiff bases (HL_1) and (HL_2)

4,4-dimethyl amino- benzylidene- amino phenol (HL_1): prepared by the condensation of (1g, 0.0067mol) 4-dimethylaminobenzaldehyde with (0.73g, 0.0067mol) 4-aminophenol in (20ml) methanol and added 3 drops hydrochloride acid as a catalyst. The mixture was refluxed for 1h with stirring. The product was dried and recrystallized from hot ethanol) (at room temperature. yield 72.5%, mp 272ºC. The^{1}H-NMR (Fig. 1) (DMSO, ppm): 9.733 (s, –CH═N, 1H), 7.838 to 8.135 (m, aromatic), 6.373(s, –OH, 1H), 3.33-3.513 (m N-$(CH_3)_2$, 6H), 3.39 (s, CH_3, 3H), (2.5, DMSO). FT-IR (cm^{-1}): 3076 (CH aromatic), 1689 (HC═N stretching) 1589, (C═C). 3414 (-OH).

2, 4-dimethylamino-benzylidene-aminophenol (HL_2): prepared by the condensation of (1g, 0.0067mol) 4-dimethylaminobenzaldehyde with (0.73g, 0.0067mol) 2-aminophenol in (20ml) methanol and added 3 drops Hydrochloride acid as a catalyst. The mixture was refluxed for 1h with stirring. The product was dried and recrystallized from hot ethanol) (at room temperature. Yield 70 %, mp 127ºC. ^{1}H-NMR (Figure 2) (DMSO, ppm):

9.333s,(HC═ N, 1H),7.838 to 8.335 (m, aromatic), 6.023 (s, –OH, 1H), 3.337 to 3.533 (m N-(CH3)2,6H), (2.5,DMSO).FTIR (Figure 2) (cm^{-1}): 3040 (CH aromatic), 1678(HC═N stretching) 1589, (C═C), 3583(-OH)

Synthesis of Schiff base complexes

The following general procedures were used. A hot ethanolic solution (30 mL) of HL_1 (0.0082 mol, 2 g) HL_2 (0.0074 mol, 2 g) and a hot ethanolic solution (30 mL) of the divalent metal salts $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.6H_2O$ (0.0041 mol) were mixed and heated under reflux for 2 h with occasional stirring. The reaction mixture was then concentrated by rotary evaporation under reduced pressure until the onset of precipitation of the product, which was separated and washed successively with H_2O, warm ethanol and diethyl ether followed by drying in vacuum over anhydrous calcium chloride and its complexes analysis, colors, and yields for the complexes are given in table 1.

Programs used in theoretical calculation

Hyper-Chem-8 is a versatile molecular modeler and editor and a powerful computational package. It offers many types of molecular and quantum mechanics calculations.

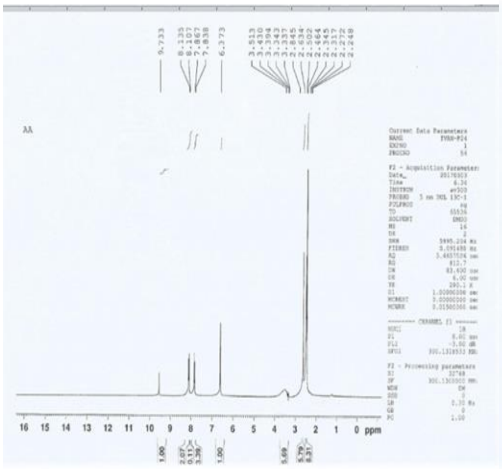


Figure 1: ^{1}H-NMR spectrum of ligand HL_1

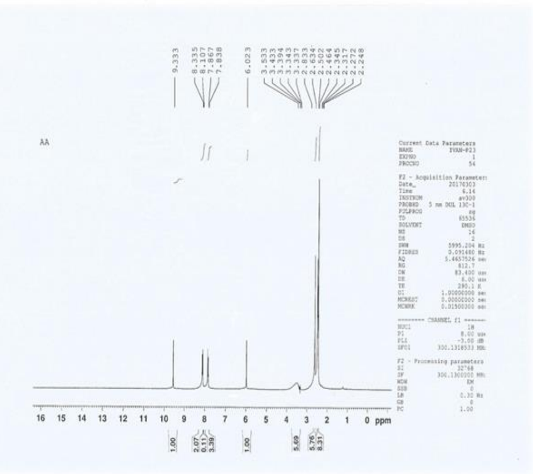


Figure 2: ^{1}H-NMR spectrum of ligand HL_2

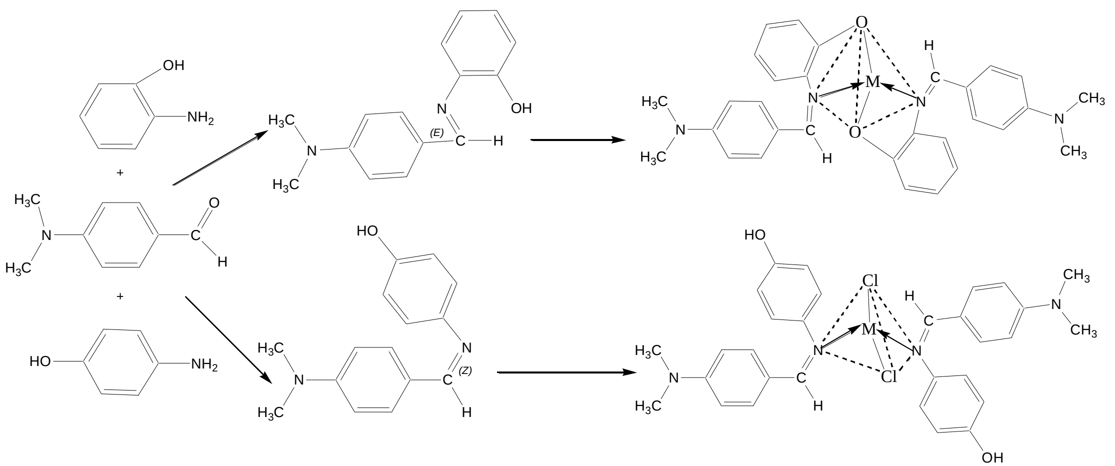
RESULTS AND DISCUSSION

All the complexes are powder, insoluble in water, whereas soluble in solvents such as, DMF, and DMSO. The molar conductance data table 1, indicate that all the complexes are non-electrolytes, Scheme 1. The ligands were characterized by elemental microanalysis and physical properties table 1, IR table 2, and UV-Vis table 3, respectively. Monomeric complexes of the ligand with [$CoCl_2.6H_2O$, $NiCl_2.6H_2O$, and CuCl2.2H2O] were synthesized by heating (0.0041mol) of the ligand with (0.0041mol) of metal salt using methanolic solution. However, deprotonation of the ligand occur facilitating the formation of the complexes The complexes are air-stable solids, solution in DMF and DMSO, sparingly soluble in MeOH, Ethanol. The analytical data table 1, agree well with the suggested formulae. The most important infrared bands of the ligands and its complexes together with their assignments are collected in table 2.

Table 1: Elemental microanalysis results and some physical properties of the ligands and their metal complexes

Com.	Formula M.wt	m.p. °C	Color	Elemental microanalysis experimental (theoretical)%					Molar Conductivity (cm^2•Ω^{-1}•mol^{-1})
				C	H	N	M	Cl	
HL_1	$C_{15}H_{16}N_2O$ 240.30	272	Dark Yello	75.81 (74.97)	6.05 (6.71)	13.01 (11.66)			-

			w						
CoL_1	$CoC_{30}H_{32}N_4O_2Cl_2$ 608.19	245	Brown	60.31 (59.19)	4.98 (5.26)	10.89 (9.20)	10.11 (9.68)	10.98 (11.6)	11
NiL_1	$NiC_{30}H_{32}N_4O_2Cl_2$ 607.85	216	Orange	60.01 (59.23)	4.88 (5.26)	10.78 (9.21)	9.98 (9.66)	10.55 (11.68)	9
CuL_1	$CuC_{30}H_{32}N_4O_2Cl_2$ 612.8	250	Black	58.08 (58.74)	4.78 (5.22)	11.01 (9.13)	10.13 (10.36)	11.01 (11.5)	12
HL_2	$C_{15}H_{16}N_2O$ 240.13	127	Yellow	75.98 (74.97)	7.01 (6.71)	13.05 (11.66)	–	–	
CoL_2	$CoC_{30}H_{32}N_4O_2$ 537.19	85	Brown	66.86 (67.01)	5.96 (5.95)	11.86 (10.42)	10.01 (10.97)	Nil	15
NiL_2	$NiC_{30}H_{32}N_4O_2$ 536.95	62	Black	66.09 (67)	6.08 (5.95)	11.81 (10.4)	12.01 (10.93)	Nil	8
CuL_2	$CuC_{30}H_{32}N_4O_2$ 541.8	199	Black	65.88 (66.45)	6.08 (5.91)	12.03 (10.34)	12.07 (11.73)	Nil	10



M(II)= Co, Ni and Cu

Scheme 1: Preparation of ligands and complexes

IR spectra

FTIR data for the ligands and metal complexes are given in table 2. infrared of HL_1 shows characteristic bands at 3414 cm^{-1} that could be attributed to the phenolic hydroxyl group, and the characteristics absorption at 1689 cm^{-1} can be assigned to (C=N)of iminic group stretching vibrationrespectively indicating the formation of the free Schiff base product.. The spectra of the complexes showed absorption bands at 497, 532 can be assigned to (Co-O, Co-N)respectively indicating the formation CoL_1.The spectra of the complexes showed absorption bands at 455, 498, 532 can be assigned to (Ni-O, Ni-N) respectively indicating the formation NiL_1.The spectra of the complexes showed absorption bands at 455, 498, 528 can be assigned to (Cu-O, Cu-N) respectively indicating the formation CuL_1.[7,9]

HL_2 shows characteristic bands at 3583 cm^{-1} that could be attributed to the phenolic hydroxyl group, and the characteristics absorption at 1678 cm^{-1} can be assigned to (C=N) of iminic group stretching vibration respectively indicating the formation of the free Schiff base product.The spectra of the complexes showed absorption bands at 497, 436, 532 and 567 can be assigned to (Co-O, Co-N) respectively indicating the formation CoL_2. The spectra of the complexes showed absorption bands at 432, 486 and 536, can be assigned to (Ni-O, Ni-N) respectively indicating the formation NiL_2. The spectra of the complexes showed absorption bands at 455, 436, 532and 490can be assigned to (Cu-O, Cu-N) respectively indicating the formation CuL$_2$ [6-8,15].

Table 2: Infrared spectral data of the free ligands and their complexes in (cm^{-1})

compounds	C=N	O-H	M-N	M-O	Other bands
HL$_1$	1689	3414	-	-	υ(C–H) =3076 arom υ(C–H) = 2981aliph
CoL$_1$	1608	3367	532	497	υ(C–H) = 3055 arom υ(C–H) =2947 aliph
NiL$_1$	1608	3372	532	455 498	υ(C–H) = 3055 arom υ(C–H) = 2974aliph
CuL$_1$	1647	3340	528	455 498	υ(C–H) = 3051 arom υ(C–H) = 2974aliph
HL$_2$	1678	3583	-	-	υ(C–H) = 3040 arom υ(C–H) = 2905aliph
CoL$_2$	1651	3583	532	497 436	υ(C–H) = 3055 arom υ(C–H) =2936 aliph
NiL$_2$	1643	3583	536	432 486	υ(C–H) =3094 arom υ(C–H) =2932 aliph
CuL$_2$	1646	3583	532 490	455 436	υ(C–H) = 3071 arom υ(C–H) =2974 aliph

UV-Vis spectral Data of ligands and their metal complexes:

The U.V-Vis. spectra of ligands and complexes explain in table (3) .The spectrum of HL$_1$ Fig. 3 displayed absorption peak high intensity appeared at (347nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition. while absorption peak weak intensity at (261nm) may be assigned to ($\pi\rightarrow\pi^*$) electronic transition .The spectrum of CoL$_1$ displayed three absorption peaks, the first peak at (799) nm may be assigned to ($^4A_2\rightarrow{}^4T_1(p)$) , second peak at (344nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition, while third peak at(272nm) may be assigned to ($\pi\rightarrow\pi^*$).The spectrum of NiL$_1$ displayed one absorption peak at (446nm) may be assigned to ($^3T_1\rightarrow{}^3T_1(p)$), second peak at (344nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition, while third peak at (275nm) may be assigned to ($\pi\rightarrow\pi^*$). The spectrum of CuL$_1$ Fig.4 displayed one absorption peak at (496nm) may be assigned to ($^2T_2\rightarrow{}^2E$), second peak at (344nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition, while third peak at (276nm) may be assigned to ($\pi\rightarrow\pi^*$).

The spectrum of HL$_2$ displayed absorption peak high intensity appeared at (423nm), (352nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition. while absorption peak weak intensity at (286nm) may be assigned to ($\pi\rightarrow\pi^*$) electronic transition, The spectrum of CoL$_2$ displayed four absorption peaks, the first peak at (729nm) may be assigned to($^4A_2\rightarrow{}^4T_1(p)$),second peak at (435nm) may be assigned to ($n\rightarrow\pi^*$+C.T) electronic transition, third peak at(345nm) may be assigned to ($n\rightarrow\pi^*$),forth peak at (281nm) may be assigned to ($\pi\rightarrow\pi^*$) electronic transition. The spectrum of NiL$_2$ displayed one absorption peak at (786nm) may be assigned to ($^3T_1\rightarrow{}^3T_1(p)$), second peak at (446nm) may be assigned to ($n\rightarrow\pi^*$+C.T) electronic transition, while third peak at (344nm) may be assigned to ($n\rightarrow\pi^*$). The spectrum of CuL$_2$ displayed four absorption peaks, the first peak at (729nm) may be assigned to ($^2T_2\rightarrow{}^2E$), second peak at (435nm) may be assigned to ($n\rightarrow\pi^*$+C.T) electronic transition, third peak at (346nm) may be assigned to ($n\rightarrow\pi^*$), while forth peak at (300nm) may be assigned to ($n\rightarrow\pi^*$) electronic transition [7, 9, 16,17].

Table 3: Electronic spectral data of the ligands and their metal complexes

Compounds	**ABS**	**λ (nm)**	**ύ (cm^{-1})**	**ε_{max} L.mol^{-1}.cm^{-1}**	**Electronic transition**	**μ_{eff}(B.M)**
HL$_1$	2.000 0.392	347 261	28818.44 38314.17	2000 392	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	
CoL$_1$	0.023 2.123	799 344	12515.64 29069.76	23 2123	$^4A_2\rightarrow{}^4T_1(p)$ $n\rightarrow\pi^*$	3.87

	0.426	272	36764.70	426	π →π*	
NiL_1	0.540	446	22421.52	540	$^3T_1 \rightarrow {}^3T_1$(p)n→π*	2.88
	2.219	344	29069.76	2219	π →π*	
	0.329	275	36363.63	329		
CuL_1	0.073	496	20161.2	73	$^2T_2 \rightarrow {}^2E$	1.77
	2.078	344	29069.76	2078	n→π*	
	0.783	276	36231.88	783	π →π*	
HL_2	0.402	423	23640.66	402	n→π*	
	1.401	352	28409.09	1401	n→π*	
	0.206	286	34965.03	206	π →π*	
CoL_2	0.007	729	13717.42	7	$^4A_2 \rightarrow {}^4T_1$(p)	3.87
	0.385	435	22988.50	385	n→π*+C.T	
	1.673	345	28985.50	1673	n→π*	
	0.261	281	35587.18	261	π →π*	
NiL_2	0.019	786	12722.64	19	$^3T_1 \rightarrow {}^3T_1$(p)	2.83
	0.549	446	22421.52	549	n→π*+C.T	
	2.219	344	29069.76	2219	n→π*	
CuL_2	0.007	729	13717.42	7	$^2T_2 \rightarrow {}^2E$	1.73
	0.385	435	22988.50	385	n→π*+C.T	
	1.437	346	28901.73	1437	n→π*	
	1.222	300	33333.33	1222	n→π*	

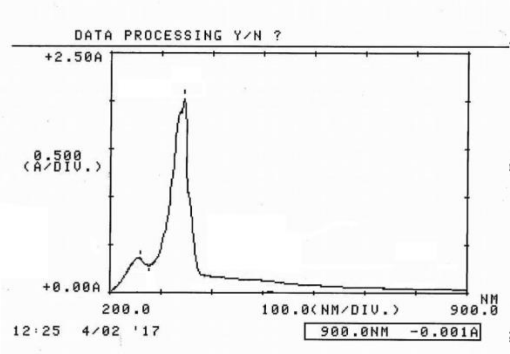


Figure 3 UV-Vis Spectrum of HL_1

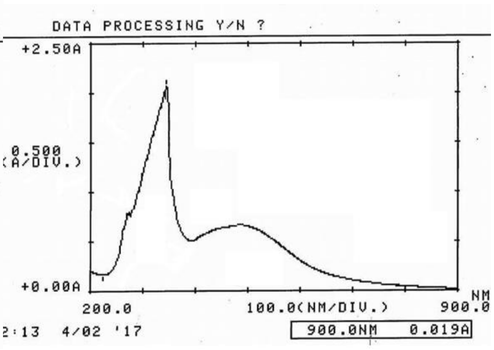
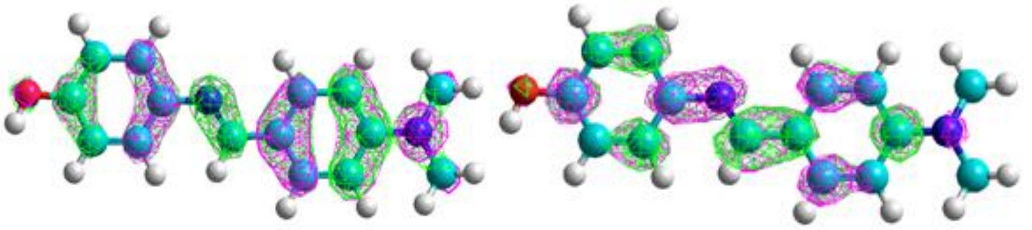


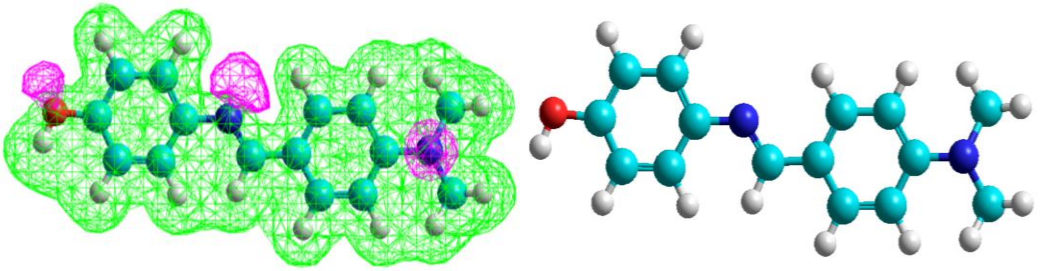
Figure 4 UV-Vis Spectrum of complex CuL_1

Electrostatic potentials

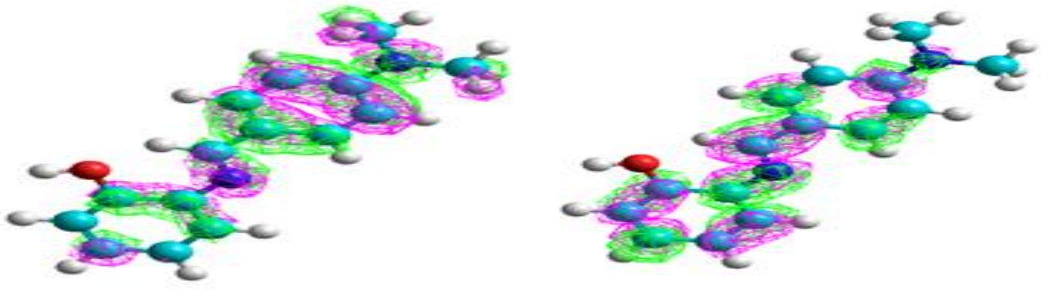
Electron distribution governs the electrostatic potential of the molecules. The electrostatic potential (E.P) describes the interaction of energy of the molecular system with a positive point charge. (E.P) is useful for finding sites of reaction in a molecule; positively charged species tend to attack a molecule where the electro static potential is strongly negative (electrophonic attack) [17]. The (E.P) of the free ligands ware calculated and plotted as 2D contour to investigate the reactive sites of the molecules, Fig.5. Also one can interpret the stereochemistry and rates of many reactions involving “soft” electrophiles and nucleophiles in terms of the properties of frontier orbital (HOMO, highest occupied molecular orbital) and (LUMO, lowest unoccupied molecules). The results of calculations show that the LUMO of metal ions prefer to react with the HOMO of two-donor atoms with nitrogen of azomethine and oxygen of the hydroxyl group for free ligands. All theoretically probable structures of free ligands and their complexes have been calculated by (PM3) and(ZINDO/1) methods in the gas phase to search for the mostprobable model building stable structure, table 5.The vibrational spectra of the free ligands and their metal complexes have been calculated, table 6. The theoretically calculated wave numbers for these ligands and their metal complexes showed that some deviations from the experimental values, these deviations are generally acceptable in theoretical calculations [18]. The most diagnostic calculated vibrational frequencies were chosen for the assignment of ligands and metal complexes which are included in table 6 and their respective experimental vibrational modes are shown in the same table 2. The results obtained for the theoretical calculations of the frequencies agreed well with those obtained for the experimental values, tables 2.



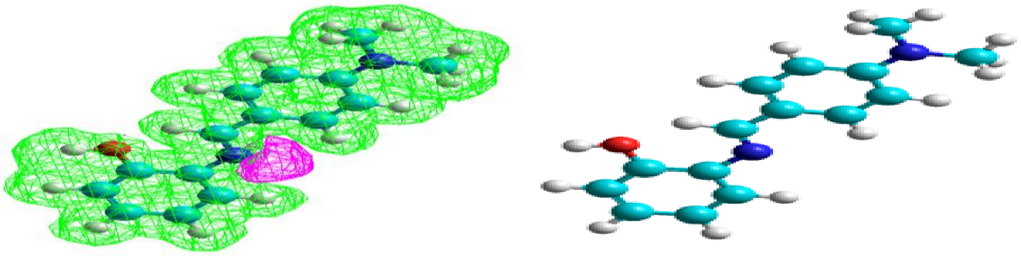
HOMO= -8.237198 ev LUMO= -0.5743506 ev



HL₁ Ligand



HOMO= -7.8101811 ev LUMO= -0.3812509 ev



HL₂ Ligand

Figure 5: Electrostatic potential (HOMO and LUMO) as 2D contours for ligands

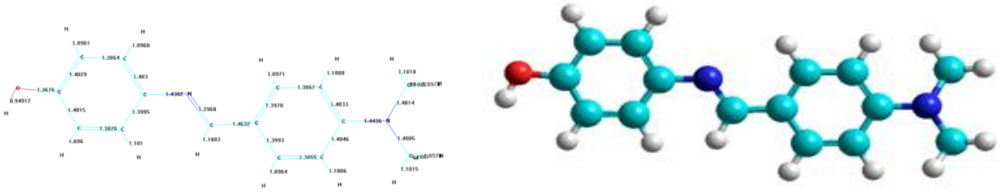
Table 4: Conformation energetic (in kJ.mol-1) for free ligands and their metal complexes

Comp.	Total energy	Binding energy (ΔE_b)	Heat of formation (ΔH°_f)	Electronic energy	Dipole (Debyes)	Isolated Atomic Energy
HL_1	-60904.4196	-3662.6821	19.85885	-390229.0332	2.614	-57241.73746
HL_2	-60897.04892	-3655.311457	27.2295422	-397859.6542	1.865	-57241.73746
CuL_1	-143201.435	-7643.115	-160.1154	-336650.011	16.611	-578870.1132
NiL_1	-192681.445	-8877.661	-188.337	-123569.432	13.311	-671150.3445
CoL_1	-177810.432	-3367.654	-200.1122	-323665.115	21.239	-555013.6623
CuL_2	-149876.321	-1323.441	-168.635	-1400054.41	11.176	-178501.054
NiL_2	-145221.9630	-7543.84965	-180.17165	-1300507.489	13.786	-137678.1134
CoL_2	-151604.187	-8876.543	-170.168	-1289460.411	12.811	-127965.115

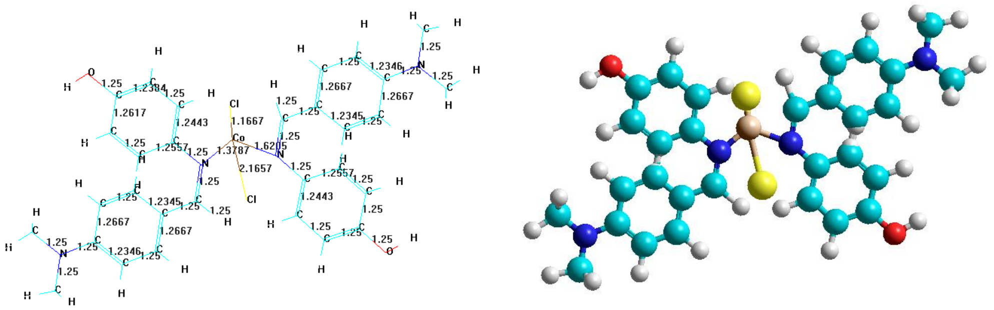
Table 5: Comparison between the experimental and theoretical vibational frequencies (cm^{-1}) for free ligands and their metal complexes

Comp.	υ(OH)	υ(CH) aromatic	υ(CH) aliphatic	υ(CH) aldehyde	υ(C=N)	υ(M-N),υ(M-O)
HL_1	3500* 3414**	3056* 3076**	2997* 2981**	2871* 2889**	1668* 1689**	______
CoL_1	3380* 3367**	3056* 3055**	2997* 2974**	2771* 2785**	1618* 1608**	590*, 501* 532**,497**
NiL_1	3360* 3372**	3056* 3055**	2997* 2974**	2871* 2880**	1620* 1608**	600*, 500* 532**,455**,498**
CuL_1	3400* 3340**	3056* 3051**	2997* 2974**	2811* 2808**	1628* 1647**	555*, 488* 528**,455**,498**
HL_2	3555* 3583**	3009* 3040**	2997* 2905**	2798* 2816**	1664* 1678**	____
CoL_2		3099* 3055**	2889* 2936**	2787* 2828**	1668* 1651**	579*,500*,485* 567**,532**,497**,436**
NiL_2		3100* 3094**	2978* 2932**	2825* 2874**	1641* 1643**	600*, 501*,470* 536**, 486**,432**
CuL_2		3100* 3071**	2978* 2974**	2825* 2885**	1641* 1646**	600*, 501*,470* 532**,490**,455**,436**

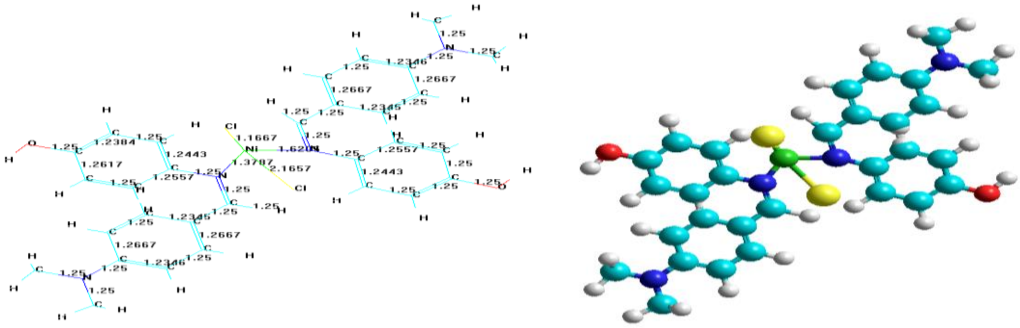
Where:-*Theoretical frequency; **Experimental frequency



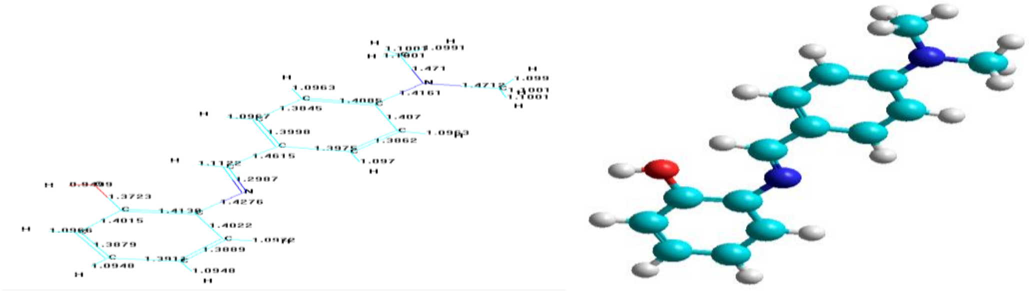
HL_1



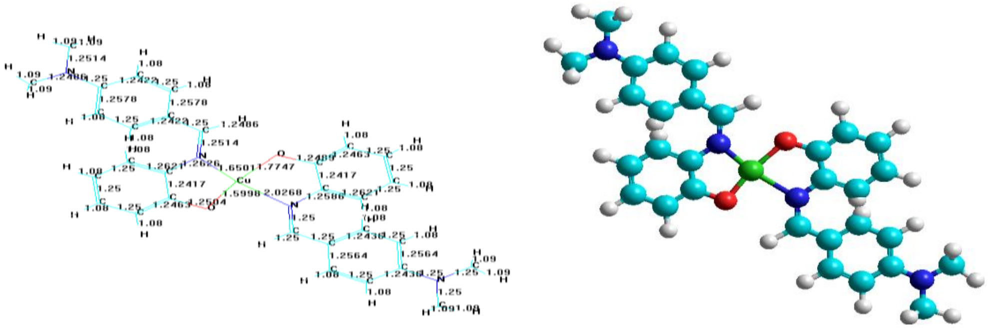
CoL_1



NiL_1



HL_2



CuL_2

Figure 6: Conformational structure of ligands and their metal complexes

Bond length measurements for the ligands and their metal complexes:

Calculation of parameters has been optimized bond lengths of the free ligands and their metal complexes by applying the Semi-empirical (PM3) at Geometry Optimization (0.001 K.Cal.mol^{-1}), which to give excellent agreement with the experimental data [19] as shown in table 7.

Table 6: Selected bond lengths (A°) for (E) ligands and their metal complexes

Compounds	C=N	C-O, O-H	M-N	M-O	M-Cl
HL_1	1.4302	1.3676, 0.949	-	-	-
CoL_1	1.25	1.25, 0.96	1.620,1.3378	-	1.1667,2.1657
NiL_1	1.254	1.25, 0.96	1.620,1.3378	-	1.1667,2.1657
CuL_1	1.251	1.25, 0.96	1.620,1.3378	-	1.1667,2.1657
HL_{32}	1.2987	1.3723, 0.9499	-	-	-
CoL_2	1.25	1.2489,-	2.0268,1.6501	1.599,1.7747	-
NiL_2	1.2942	1.3245,-	1.834,1.8338	1.8501,1.8506	-
CuL_2	1.25	1.2489,-	2.0268,1.6501	1.7747,1.5998	-

Theoretical electronic spectra for the metal complexes

The electronic spectra of the metal complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values as shown in table 8. These deviations in theoretical calculation are generally acceptable due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam [20]. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes. Experimental electronic modes are shown in table 8. All the theoretical electronic spectra of all compounds were calculated by using the semi-empirical (PM3) method at geometry optimization (0.01 K. Cal. Mol^{-1}) was used, and the comparison between of the experimental data and theoretical data of the electronic spectra for metal complexes in table 8.

Table 7: Comparison between experimental and theoretical of the electronic spectra for complexes

Complexes	Maximum absorption(nm)		Band assignment	Suggested geometry
CoL_1	799*	801	$^4A_2 \rightarrow ^4T_1(p)$	Tetrahedral
NiL_1	446*	454	$^3T_1 \rightarrow ^3T_1(p)$	Tetrahedral
CuL_1	496*	500	$^2T_2 \rightarrow ^2E$	Tetrahedral
CoL_2	729*	774	$^4A_2 \rightarrow ^4T_1(p)$	Tetrahedral
NiL_2	786*	778	$^3T_1 \rightarrow ^3T_1(p)$	Tetrahedral
CuL_2	729*	745	$^2T_2 \rightarrow ^2E$	Tetrahedral

Where: *Theoretical frequency; **Experimental frequency

Antioxidant activity of the ligand and metal complexes by DPPH method:

Each of the Schiff bases and the metal complexes were dissolved in DMSO and ethanol to obtain concentration of (10 mmol l^{-1}). These stock solutions were then diluted to (0.2, 0.4, 0.6, 0.8 and 1 mmol.l^{-1}). While gallic acid as standard. Then, 100µL of each sample solution were mixed with 6ml of 45µg ml^{-1}DPPH that was dissolved in ethanol. The reaction mixture was incubated in the dark for (30 and 60 min) at room temperature when DPPH reacts with an antioxidant compound, which can donate hydrogen, it is reduced. The changes in color (from deep violet to light yellow)The DPPH radical scavenging activity was determined by measuring the absorbance at 517 nm using the UV-Vis spectrophotometer the percentage of DPPH radical scavenger was calculated using Equation 1.

$$\%\text{Inhibition} = \frac{A_{Control} - A_{Test}}{A_{Control}} \text{ x } 100 \quad [21]$$

Statistical Analysis

All the analysis were carried out in Excel and expressed as mean Standard deviation, Coefficient of variation %, Correlation coefficient and IC50 were showed in table (9,10,11), see fig 7-9.

Table 8: Means, standard deviations, coefficients of variation, Correlation coefficient and IC50 of antioxidant activity in percentage (aa%) of the tested samples at 30. minute.

Tested Samples	Mean	Standard deviation	Coefficent of varation %	Correlation coefficient	IC50
HL_1	63.8	26.93434982	42.21684924	0.984075954	0.372
CoL_1	90.78	3.622963796	3.990927292	0.996650939	
NiL_1	75.5	19.61065017	25.97437108	0.984075954	
CuL_1	42.96	7.792235452	18.13835068	0.999916677	0.958
HL_2	82.42	5.497878379	6.67056343	0.974990301	
CoL_2	70.76	11.18026833	15.80026616	0.965431736	
NiL_2	87.04	2.828427125	3.249571605	0.993694405	
CuL_2	32.12	4.784196206	14.8947578	0.880776143	1.595

Where IC50:the half maximal inhibitory concentration

Table 9: Means, standard deviations, coefficients of variation, Correlation coefficient and IC50 of antioxidant activity in percentage (aa%) of the tested samples at 60. minute.

Tested Samples	Mean	Standard deviation	Coefficient of variation %	Correlation coefficient	IC50
HL_1	59.632	25.37284217	42.54903772	0.991076671	0.478
CoL_1	87.8325	3.213838567	3.659053957	0.963347386	
NiL_1	72.14	10.32142109	14.30748696	0.980670469	
CuL_1	52.24	9.680771319	18.53133867	0.99840333	0.47
HL_3	79.52	5.800229881	5.134071356	0.985283505	
CoL_3	73.72	8.791875037	11.92603776	0.985150419	

NiL_3	88.52	4.97696025	5.622413297	0.94904442	
CuL_3	44.22	11.51692088	26.04459721	0.989130266	0.631

Where IC50:the half maximal inhibitory concentration

Table 10: Means, standard deviations, coefficients of variation, Correlation coefficient and IC50 of antioxidant activity in percentage (aa%) of the Gallic acid at 30. minute.

Tested Sample	Mean	Standard deviation	Coefficient of variation %	Correlation coefficient
Gallic acid	95.056	2.382200663	2.506102364	0.992940572

Table 11: Means, standard deviations, coefficients of variation, Correlation coefficient and IC50 of antioxidant activity in percentage (aa%) of the Gallic acid at 60. Minute

Tested Sample	Mean	Standard deviation	Coefficient of variation %	Correlation coefficient
Gallic acid	95.488	1.789390958	1.873943279	0.99672159

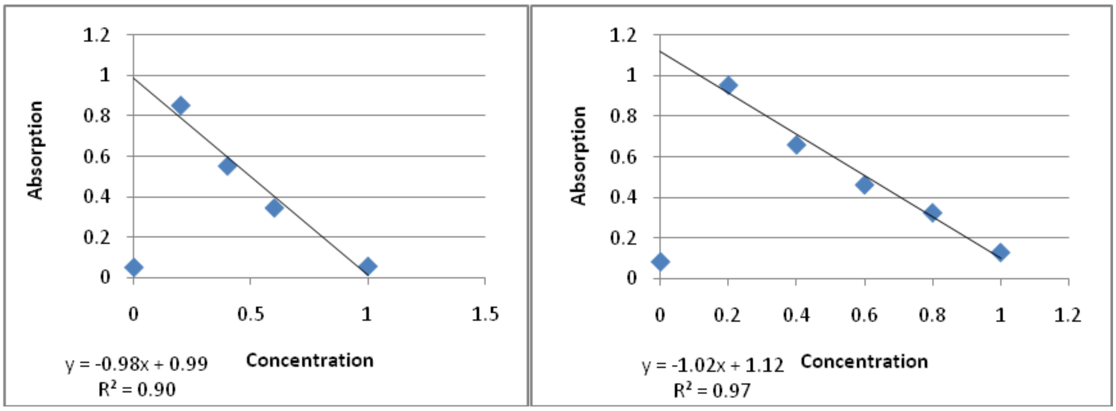
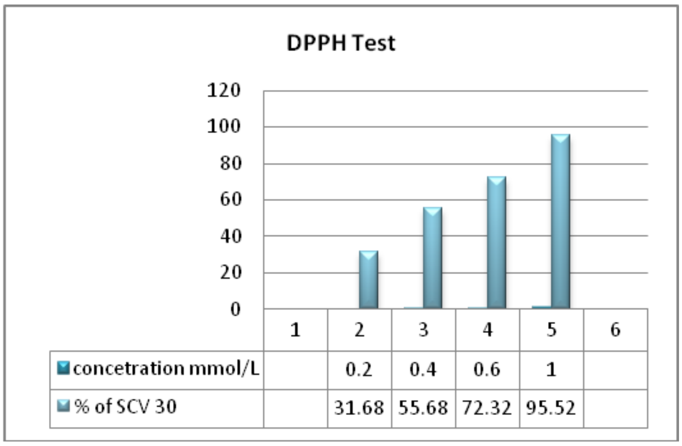


Figure 7 Standard curve of HL_1 at 30 and 60min.



	1	2	3	4	5	6
concetration mmol/L		0.2	0.4	0.6	1	
% of SCV 30		31.68	55.68	72.32	95.52	

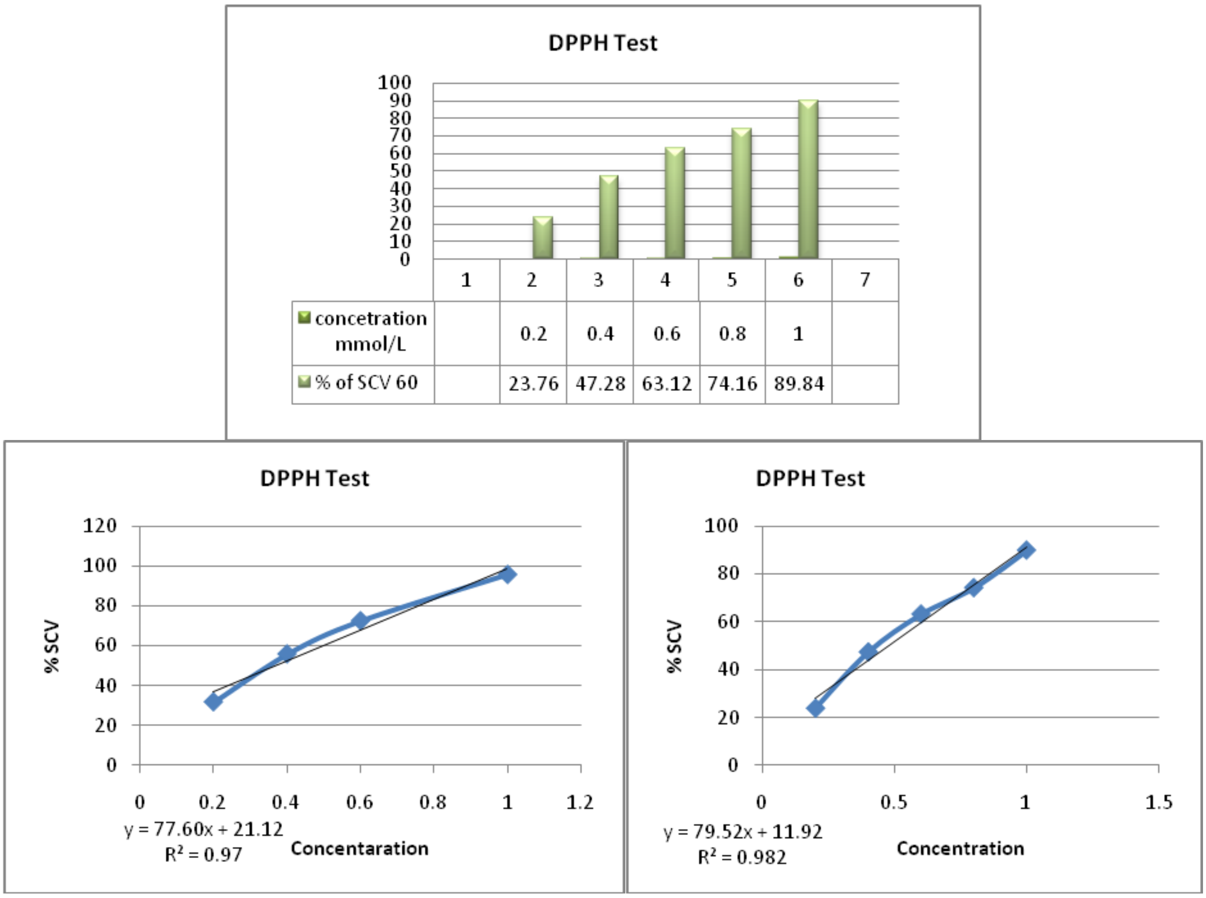


Figure 8: DPPH scavenging activity of HL_1 ligand at 30 and 60 min.

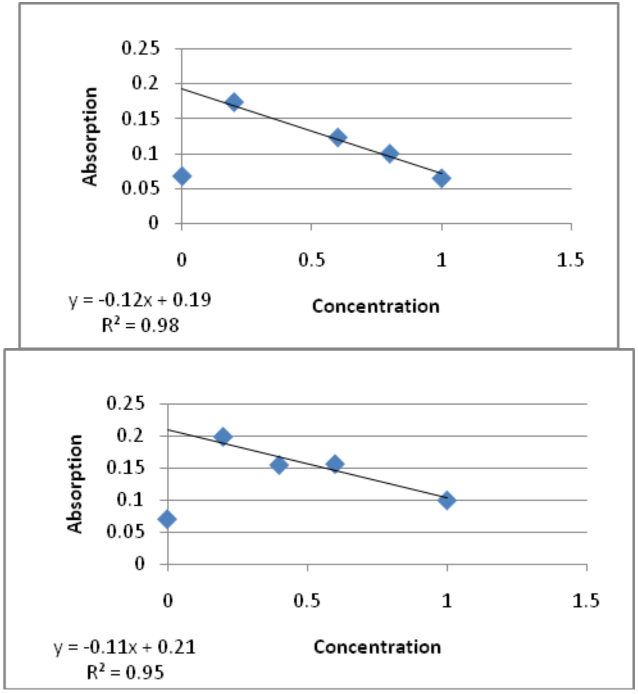


Figure 9 Standard curve of CoL_1 complex at 30 and 60min.

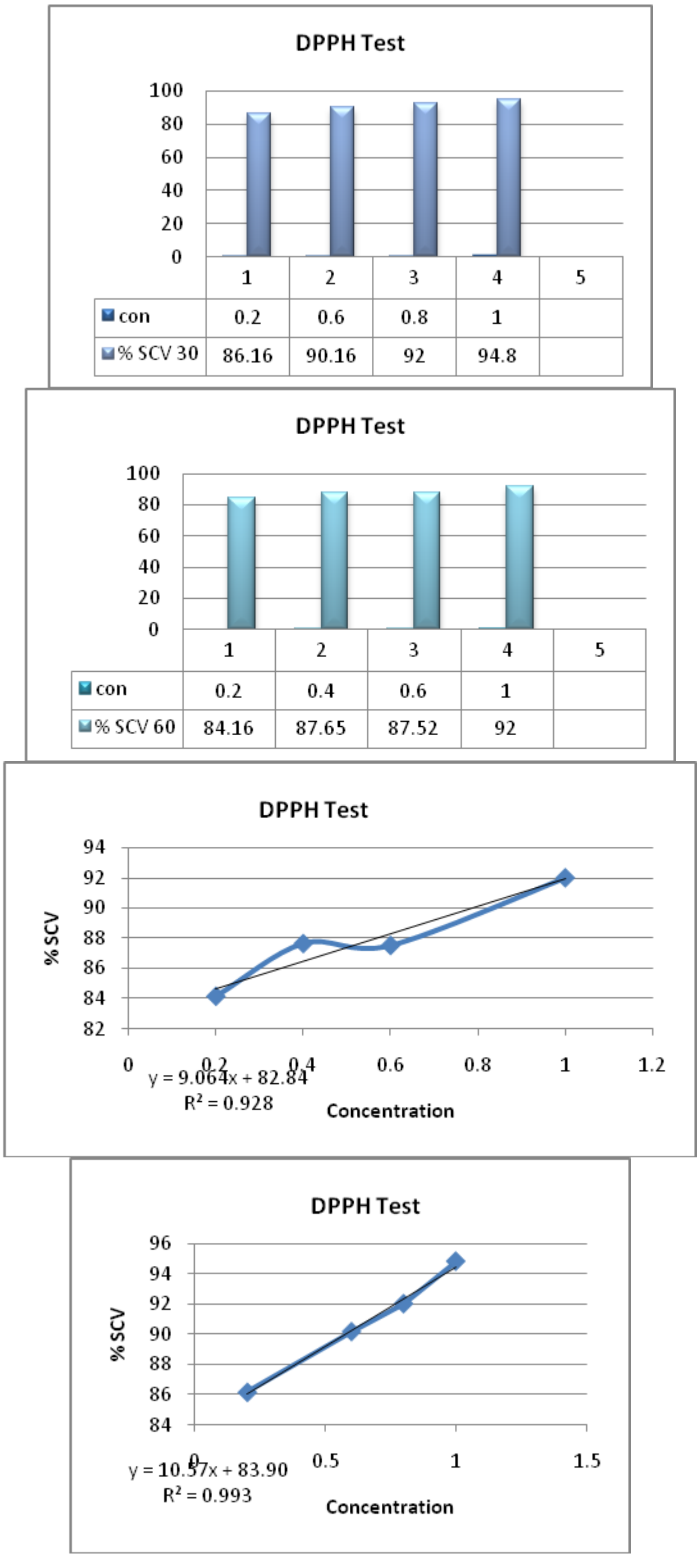


Figure 10: DPPH scavenging activity of CoL_1 complex at 30 and 60 min

CONCLUSION

In this paper we prepared ligands. (4, 4- dimethyl amino- benzylidene) - amino phenol) and (2, 4-dimethylamino-benzylidene)-aminophenol)which were used in the preparation of Co(II) Ni(II) and Cu(II) complexes characterization data by FT.IR, ^{1}H-NMR, UV-Vis spectrometer, element microanalysis (C.H.N.), melting point for free Schiff base ligands and FT.IR, UV-Vis spectrometer, element micro analysis (C.H.N) magnetic susceptibility, molar conductivity, atomic absorption, chloride content, melting point for complexes. Theoretical studies of their gas phase by semi-empirical method in order to: Show the most stable conformation through calculating the total energy, dipole moment, electrostatic energy, heat of formation, and binding energy for all the probable geometries. Find the most active sites of the prepared ligands by using the electrostatic potential calculation and show the HOMO and LUMO position. Calculate the vibrational frequencies of the ligands and complexes with metal in order to compare the results with the experimental vibrational frequencies to make a certain assignment of the most diagnostic bands. Calculate the spectrum UV-VIS of the ligands and complexes with metal. The prepared Schiff bases and their metal complexes as antioxidant agents compared with Gallic acid, the results from DPPH and method revealed that compounds are capable of donating hydrogenatom and subsequently react with free radicals In addition, the presence of hydroxyl groups, which are attached to aromatic rings can increase the conjugated systems and consequently increase the antioxidant activity of the corresponding Schiff bases and metal complexes.

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