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New mixed ligand complexes of New Schiff base 4,4'-((naphthalen-1-ylimino) methylene) dibenzene-1,3-diol and 8-hydroxy quinoline: Synthesis, Spectral Characterization, Thermal studies and Biological Activities

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Abstract

A new bidentate Schiff base ligand has been synthesized with the use of 2,2,4,4-tetrahydroxybenzophenone and1-naphthylamine. Its mixed ligand complexes of (MAQ) types [M= Mn (II),Co(II),Cu(II),Zn(II),Cd(II)and Hg(II); (HA)=Schiff base and (HQ)=8-hydroxy quinoline] . Ligand (HA) and complexes have been identified with the spectroscopic and analytical analyses including; micro-analysis, thermal analyses, chloride content, conductance, magnetic susceptibility for complexes, UV-Visible, FTIR, and 1H,13C-NMR spectroscopy. The physico-chemical methods indicated the complexes which have been shown 4 and 6 coordinate structures in solution and solid states. The ligand (HA) binds with the ions of M(II) through azomethine and de-protonated phenolic group and ligand (HQ) binds via the azomethine in the ring and de-protonated phenolic group. Thermal analysis was used to confirm the existence of coordination H2O molecule in complexes structure. According to mentioned characterization methods, Mixed ligand complexes of bivalent ion of Mn(II), Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) of the according to formula [M(A)(Q)] in which [M= Mn(II),Zn(II),Cd(II)and Hg(II)] and the formula [M(A)(Q)(H2O)2] in which [M= Co(II)and Cu(II)] in (1:1:1) of molar ratio. In vitro biological free ligand (HA) activities, 8-hydroxy quinoline (HQ) and their metal complexes were observed for bacteria, E. coli and S. aureus by well diffusion technique.

Keywords: 8-hydroxy quinoline, benzophenone, tetrahedral, thermal analysis.

INTRODUCTION

The Schiff base metal complexes' chemistry has been one of the most interesting subjects, due to the fact that those species exhibit various modes of reactivity and they have biological and catalytic activities [1]. The Schiff bases that contain 'N', 'O' donor ligands have a significant impact on the coordination chemistry sue to the fact that they may be easily forming stable complex types with the majority of transition metal ions[2]. The benzophenone derivative Schiff bases have been stated to be showing biological activities like the cytotoxic activities against the human oral squamous carcinoma cells. The mixed ligand complexes of the transition metal ions are greatly interesting for researchers studying their behavior of coordination and exploiting their characteristics in various areas, particularly anti-bacterial activities [3-5] , 8-HQ is one of the significant compounds having the capability of coordinating with different ions as bidentate through the quinoline ring nitrogen atom and oxygen atom after the hydroxyl group de-protonation [6-9] for formatting 5 member rings between that ligand with central metal ion which is helpful for increasing the complexes' stability, in addition to its known biological activities [10] ,In the presented work a Schiff base has been prepared through condensing 2,2,4,4-tetrahydroxybenzophenone and1-naphthalamine. Using this Schiff base and 8-hydroxy quinoline six new complexes of Mn(II), Co(II), Cu (II),Zn(II),Cd(II)and Hg(II) were produced and identified by a variety of the physico-chemical approaches like the molar conductance, magnetic susceptibility, electronic spectra, FTIR spectra and examine the biological activities against a variety of the MDR bacteria species.

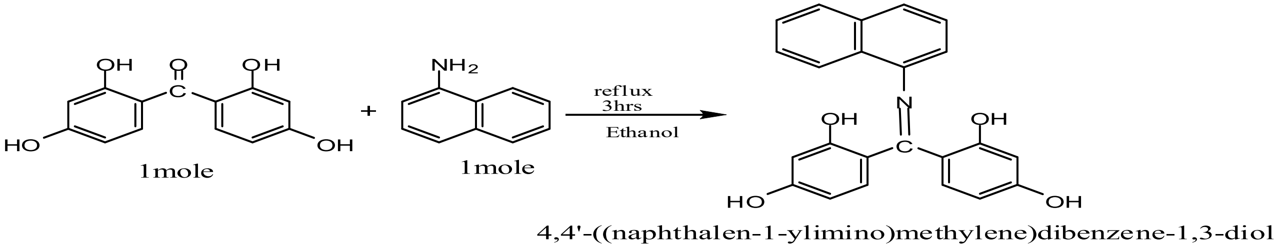
EXPERIMENTAL

MATERIALS AND METHODS

Every utilized chemical has been of an analytical grade and has been utilized with no additional purifications. Reagents have been utilized with no additional purifications as well. The FT-IR spectra have been evaluated as (KBr disc) with the use of the "Shimadzu FT-IR-8400-S", FT-IR spectro-photometer. The ^{1}HNMR and ^{13}CNMR have been performed with the use of the Bruker 400MHz NMR spectrophotometer in central lab. of Isfahan Univ., Iran. Electronic spectra have been recorded in the DMSO on "Shimadzu UV-visible160 A UV-Vis. Spectrophotometer". Elemental micro-analyses (C.H.N.) have been carried out with the use of the Leco932 US Elemental Analyzer. Atomic absorption has been evaluated with the use of "Varian-AA775 Atomic Absorption spectrophotometer". The chloride has been determined with the use of the potentiometer titration approach on a (686Titro processor-665 Dosimat-Metrohm). The evaluations of the Conductivity have been carried out in the DMSO for 10^{-3} M of the complexes with the use of the (Philips PW 9526 Digital Conductivity meter) at room temperature. Thermo-gravimetric analysis has been carried with the use of the Differential Scanning Calorimetry (DSC) on the SDT Q600 V20.9 Build 20 at Beam Gostar Lab/ Tehran Islamic Republic of Iran. Magnetic moment (μ_{eff} B.M) for prepared complexes has been measured at the temperature of the room with the use of the B.M. Ultimately, the melting points have been obtained through the use of the "Stuart Melting Point Apparatus".

Preparation of ligand Schiff Base

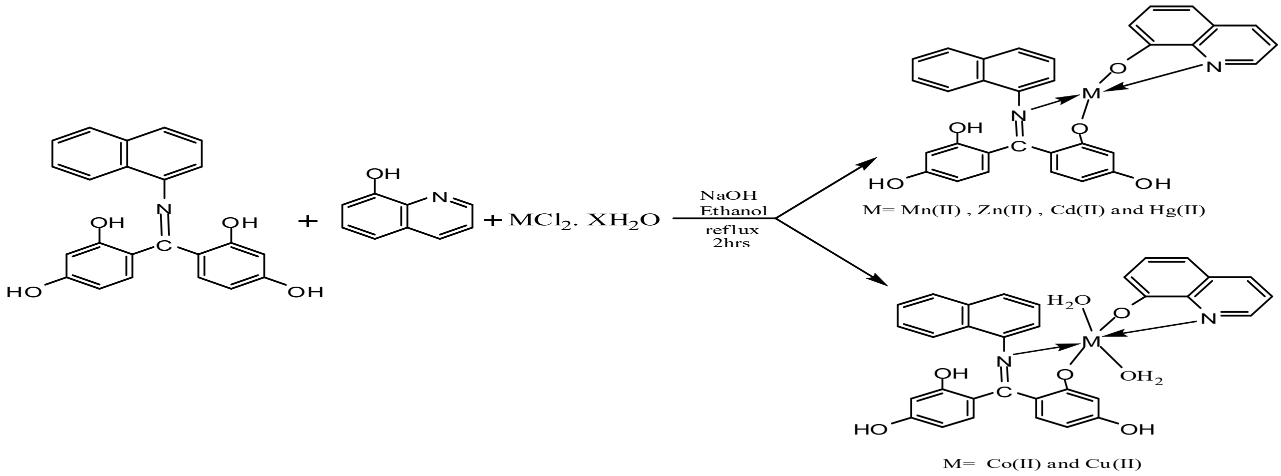
(0.1gm, 1mmole) of 2,2,4,4-tetrahydroxybenzophenone in 10ml of ethanol with (0.05 gm,1mmole) of –naphthylamine in (1:1) ratio was performed by heating under reflux (3hrs). The yellow-colored solid mass formed was cooled and then condensed solid product and isolated by filtration. The ligand synthesis route has been depicted in scheme (1). The micro-analysis of results for ligand (HA) and some of the physical characteristics have been listed in Table1.



Scheme 1. Synthesis route of ligand schiff base (HA)

General preparing of mixed ligand metal complexes

Solid complexes have been produced from mixing of (10) mmole of primary ligand (HA) for [M(A)(Q)] formula and $[M(A)(Q)(H_2O)_2]$ formula with (10) mmole of 8- hydroxyl quinoline (HQ) , and (10) mmole of the metal chloride in 25ml of the absolute ethanol. The (1)N drops of the NaOH have been added into this mix reflux the mix for (2hrs) to the formation of precipitation formed then it has been filtered, air-dried, and recryclized from the ethanol. Scheme (2) shows the overall reaction to the preparation of complexes, table1 lists some physico-chemical ligand (HA) and prepared complexes' characteristics.



Scheme 2. Syntheses of mixed ligand complexes

Table 1. The micro-analysis of results and some physical characteristics for ligand(HA) and the prepared complexes

Compounds	M. wt g.mol^{-1}	MP Dec.	Yield %	Colour	Elemental Analysis Found (Calc.) %(calc.)					Molar conductivity (S.cm^{2} molar^{1})
					C	H	N	M	Cl	
(HA)	371.39	(89-91)	85	Yellow	74.54 (74.38)	4.53 (4.61)	3.19 (3.77)	-	-	-
[Mn(A)(Q)]	569.47	267dec.	75	Brown	67.19 (67.49)	4.65 (3.89)	4.80 (4.92)	9.77 (9.65)	Nil	15.3
[Co(A)(Q) (H$_2$O)$_2$]	609.49	254dec.	69	Drak green	62.98 (63.06)	4.63 (4.30)	4.55 (4.60)	9.46 (9.67)	Nil	12.9
[Cu(A)(Q) (H$_2$O)$_2$]	614.10	236dec.	71	Brown	62.86 (62.59)	4.63 (4.27)	4.85 (4.56)	10.57 (10.35)	Nil	9.7
[Zn(A)(Q)]	579.94	252dec.	72	Pale yellow	66.45` (66.27)	3.60 (3.82)	4.68 (4.83)	11.79 (11.28)	Nil	11.6
[Cd(A)(Q)]	626.94	231dec.	65	Pale yellow	61.29 (61.30)	3.29 (3.54)	4.66 (4.47)	17.88 (17.93)	Nil	12.5
[Hg(A)(Q)]	715.12	259dec.	76	Mustard	57.56 (57.75)	3.31 (3.10)	3.77 (3.92)	28.12 (28.05)	Nil	16.2

RESULTS AND DISCUSSION

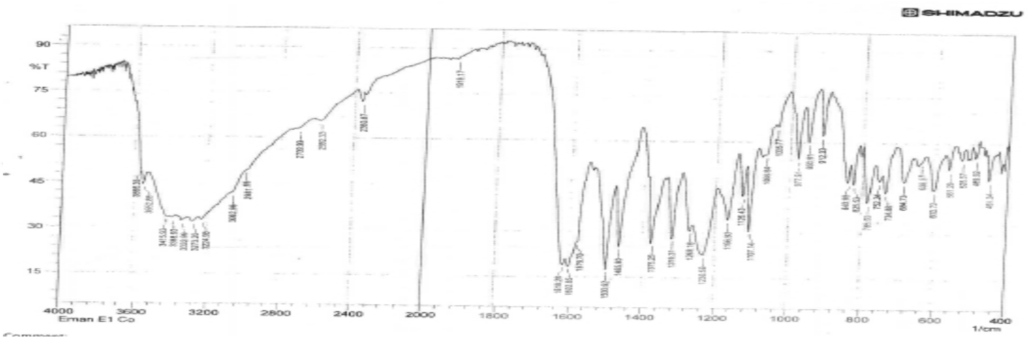
FT-IR Spectra

The FTIR Spectra of free ligands has been researched and assigned on bases of careful comparisons of complex spectra with that of free ligands, the data were tabulated in table(2).The FTIR spectra of Schiff base ligand (HA),figure(1)show a strong absorption band at (1614)cm^{-1} which is characteristic of the ν (C=N) group[11]. In spectra of all complexes, the band that has been assigned to azomethine group vibration, ν(C=N), has been shifted to higher wave numbers, which indicated the role of the atoms of nitrogen in coordinating to the ions of the metal [12]. The ν(OH) phenolic hydroxyl groups stretching frequency of the ligand (HA) expected in the range (3423–3327)cm^{-1}. A strong band observed at (1257) cm^{-1} is possibly a result of ν(C–O) stretching vibration as it has been stated for this ligand type (HA) [13]. The vibrations of ν(C–O) are shifted to higher frequency values, suggesting the fact that the metal ion coordination occurs through the phenolic *ortho*-oxygen atom as it is has been noticed for all of the transition metal complexes of *o*-hydroxy Schiff base [11,14,15]. The spectra of ligand (HQ) , show band at (3182cm^{-1}) may be a result of the ν(OH) group [16], while band at (1579) cm^{-1} can result from the ν(C=N) ring group [16].The band arising due to vibration ν(C=N) (HQ) mode at (1579cm^{-1}) frequency in free ligand (HQ) were observed to be shifted to higher frequency values and appears at (1595), (1602), (1591), (1589) and (1587)cm^{-1} for complexes Mn(II), Co(II), Cu(II), Zn(II) and Cd(II) respectively [17], while band at (1496)cm^{-1} for Hg(II) can be a result of the ν(C=N) (HQ) shifted to the lower frequency values. The observation has led to the conclusion that the complexes formation happens by the de-protonation of ν(OH) group of (HQ) moiety, suggesting the displacement of hydroxyl proton by M(II) ion leading to covalent (M-O) and (M-N) bonding with ligand (HQ) [18]. The IR spectra of Co(II) and Cu(II) complexes exhibit a broad bands in the range (3566-3224) and (3606-3261)cm^{-1} in Co(II) and Cu(II) complexes respectively, given to (OH) groups of coordinated water molecules that are related to the complexes that have been confirmed by thermal and elemental analyses[19,20]. Finally the spectra of six mixed ligand complexes showed new bands around (578-504) cm^{-1} and (491-405) cm^{-1} as a result of ν(M-N) and ν(M-O) respectively, this bands supported the formation of the complexes under investigation[21]. The characteristic FTIR data is presented in table2. The complexes' spectra have been shown in figures (1-3).

Table 2. Infrared data of ligands(HA)and (HQ)(cm^{-1}) and their complexes

Compounds	υ(OH)$_{Ph.}$	υ(OH)Qu.	υ(OH) water	ν(C=N) imine	ν(C=N) $_{ring\ Qu.}$	υ(C-H) $_{arom.}$	ν (M-N)	ν (M-O)
(HA)	(3423-3327)	-	-	1614	-	3097	-	-
(HQ)	-	3282	-	-	1579	3049	-	-
[Mn(A)(Q)]	(3373-3260)	-	-	1622	1595	3057	536 499	491 433
[Co(A)(Q) (H$_2$O)$_2$]	overlap	-	(3566-3224)	1618	1602	3062	526 489	451 408
[Cu(A)(Q) (H$_2$O)$_2$]	overlap	-	(3606-3261)	1620	1591	3066	578 509	451 424
[Zn(A)(Q)]	(3446-3273)	-	-	1627	1589	3021	512 467	435 409
[Cd(A)(Q)]	(3454-3375)	-	-	1920	1587	3035	526 493	451 441
[Hg(A)(Q)]	(3425-3252)	-	-	1622	1496	3057	504 482	455 405

Figure 1. FTIR Spectrum of the ligand Schiff base (HA)



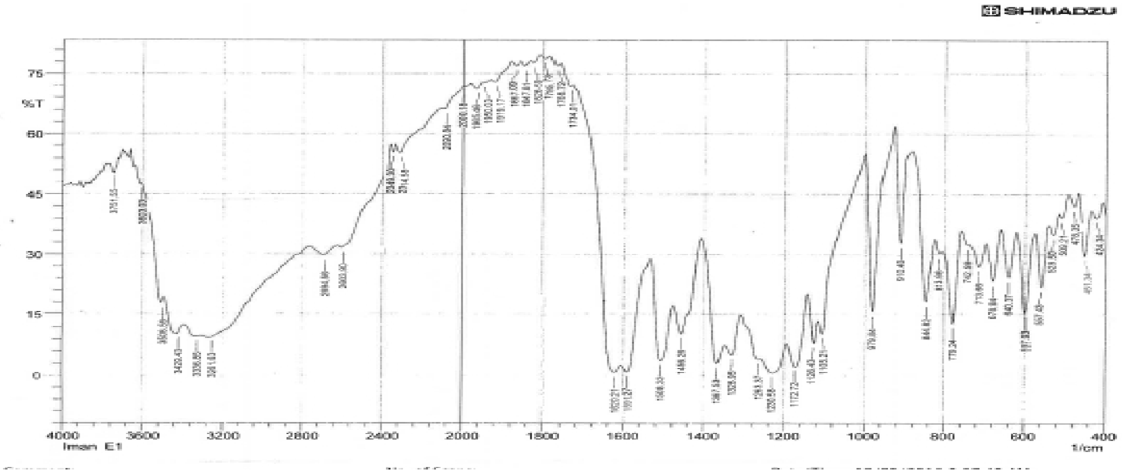


Figure 2. FTIR Spectrum of the Co complex
Figure 3. FTIR Spectrum of the Cu complex

NMR Spectra

^{1}H-NMR spectrum of ligand (HA) figure (4) has been recorded in d$_6$DMSO. ^{1}H-NMR spectra of (HA) exhibited signals because of the protons of (OH) groups as singlets at δ (13.18, 9.63) ppm [22]. ^{1}H-NMR spectrum of ligand (HA) showed a multiplet between δ (07.59-07.10) ppm may be due to aromatic protons. DMSO signal has appeared at (2.50ppm) [23]. ^{13}C-NMR spectrum of ligand (HA) figure (5), exhibits chemical shifts at (178.39ppm) refer to (C=N) group [24]. Signals that are associated with the aromatic carbons have been detected at a range (102.1- 169.8) ppm[22]. Ultimately, chemical shift at (40.20ppm) results from the DMSO d$_6$ [23].

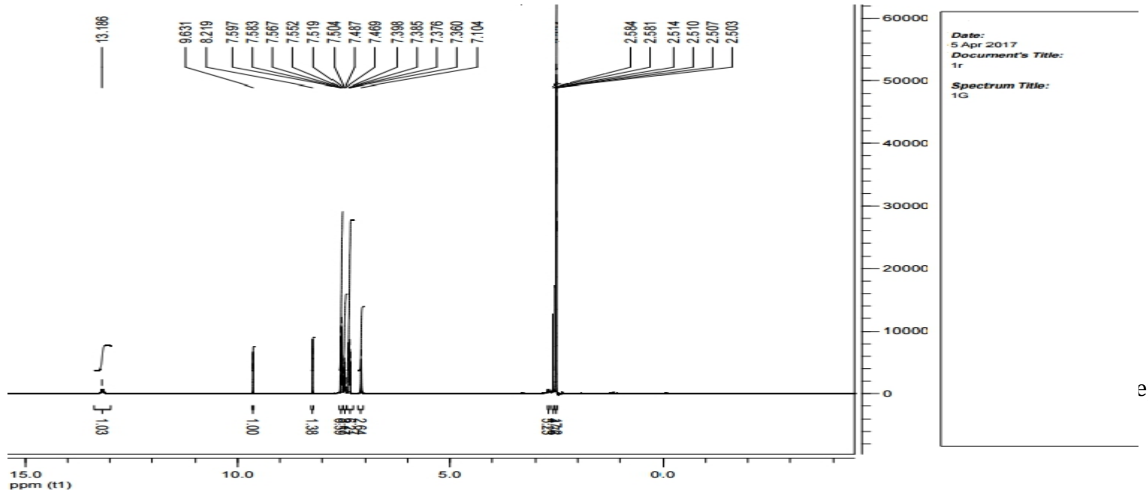


Figure 4. ^{1}H-NMR ligand (HA) spectra

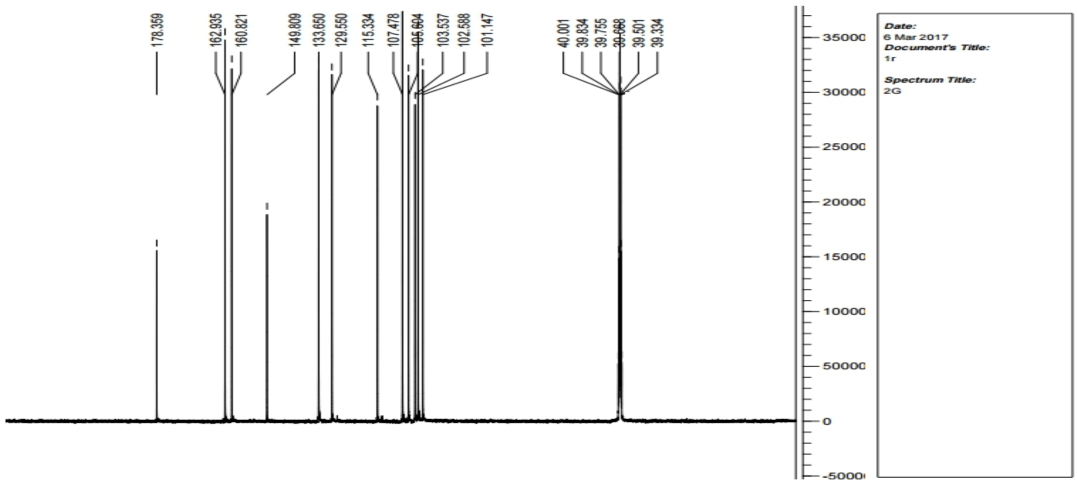


Figure 5.^{13}C-NMR ligand (HA) spectra

Electronic spectra, Magnetic moments and conductivity measurement

The electronic spectra of ligand (HA), figure(6) have exhibited high intensity peaks of absorption at (272nm & 338nm) and that has been a result of (π→ π*) & (n→ π*) transitions respectively [25], data has been listed in Table3. The electronic 8-(HQ) spectrum, figure(6) exhibits the high intensity bands of absorption at (305nm) that has been assigned to (π→ π*) & (n→π*)transitions [26], data has been listed in Table2. Electronic complexes spectra have shown a variety of the levels of bathochromic shifts of the bands at (274-278) & (341-349) nm associated with ligand field (π π*) &(n π*) transitions in complexes. The bands at (408-419) nm have been associated with the transitions of the charge transfer (C.T) in complexes [27]. The Mn(II) complex spectrum has shown a peak in d-d region at 730 nm that has been given to ($^6A_1\rightarrow{}^4E$) transition, which has indicated the tetrahedral geometry of the Mn(II) ion [28]. The value of the magnetic moment 5.57 B.M of the Mn(II) complex has been typical for the high spin Mn(II) ion that has been assigned to the tetrahedral Mn(II) complex structures [25,27]. Co(II) complex, figure(7), has exhibited an additional peak in d-d region at 550 nm and 645 nm as a result of the ($^4T_1g(F)\rightarrow{}^4T_1g(P)$) & ($^4T_1g$ (F) $\rightarrow{}^4A_2g(F)$) respective transition cases, indicating octahedral geometry around the Co atom[28]. The eff value of 4.86 B.M for the Co(II) complex has confirmed the formation of a 6-coordinate complex with an octahedral configuration about the metal center [25,27]. The Cu(II) complex spectrum has shown peaks in d-d region at 701nm and 859nm due to d-d transitions type ($^2B_2g \rightarrow {}^2B_1g$) and ($^2Eg\rightarrow{}^2T_2g$) respectively confirming octahedral geometry about the Cu atom [29]. The value of the magnetic moment of 1.74 BM for the Cu(II) complex has confirmed octahedral geometry about the ion of Cu(II) [25,27]. The electronic Zn(II) ,Cd(II) and Hg(II) complex spectra exhibited peaks at 408, 412,419 nm that assigned charge transfer transitions in Zn(II) ,Cd(II) and Hg(II) complexes, respectively [30,31].The Mn(II), Co(II), Cu(II), Zn(II) ,Cd(II) and Hg(II) complex spectra of mixed ligand complexes have shown similar behavior to these of the mixed ligand complexes which has suggested the tetrahedral geometry for [Mn(II), Zn(II), Cd(II) and Hg(II)] and octahedral geometry for the [Co(II) and Cu(II)] ions . The complexes' molar conductance in solutions of the DMSO has been an indication of their non-electrolytic natures [32,33], table1. The electronic data, and magnetic moment measurements of mixed ligand complexes in addition to their assignments have been provided in (Table3).

Table 3. Electronic spectral data (nm) of ligands as well as their metal complexes in solvent of DMSO, Magnetic moments

Compounds	λnm	Wave number Cm^{-1}	ε max (mola^{r-1}·cm^{-1})	Assignments	μeff (BM)	geometry
(HA)	272 338	36764 29585	2111 2260	π→π* n→π*	-	-
(HQ)	305	32786	1966	π→π* n→π*	-	-
[Mn(A)(Q)]	277 342 412 730	36101 29239 24271 13698	2418 2238 1368 12	L.F L.F C.T $^6A_1\rightarrow{}^4E$	5.57	Tetrahedral
[Co(A)(Q)(H_2O)$_2$]	274 314 341 415 550 645	36496 31847 29325 24096 18181 15503	1.352 1.585 1.659 248 64 56	L.F L.F L.F C.T $^4T_1g(F)\rightarrow{}^4T_1g(P)$ ^4T_1g (F) $\rightarrow{}^4A_2g(F)$	4.86	Octahedral
[Cu(A)(Q)(H_2O	276	36231	2329	L.F	1.74	Octahedral

)2]	343 412 701 859	29154 24271 14265 11641	1763 998 145 56	L.F C.T $^2B_2g \rightarrow {}^2B_1g$ $^2Eg \rightarrow {}^2T_2g$		
[Zn(A)(Q)]	278 349 412	35971 28653 24271	2216 1358 995	L.F L.F C.T	Diamagnetic	Tetrahedral
[Cd(A)(Q)]	275 34 5 408	36363 28985 24509	2315 1825 1339	L.F L.F C.T	Diamagnetic	Tetrahedral
[Hg(A)(Q)]	276 341 419	36101 29325 23866	2463 1305 1687	L.F L.F C.T	Diamagnetic	Tetrahedral

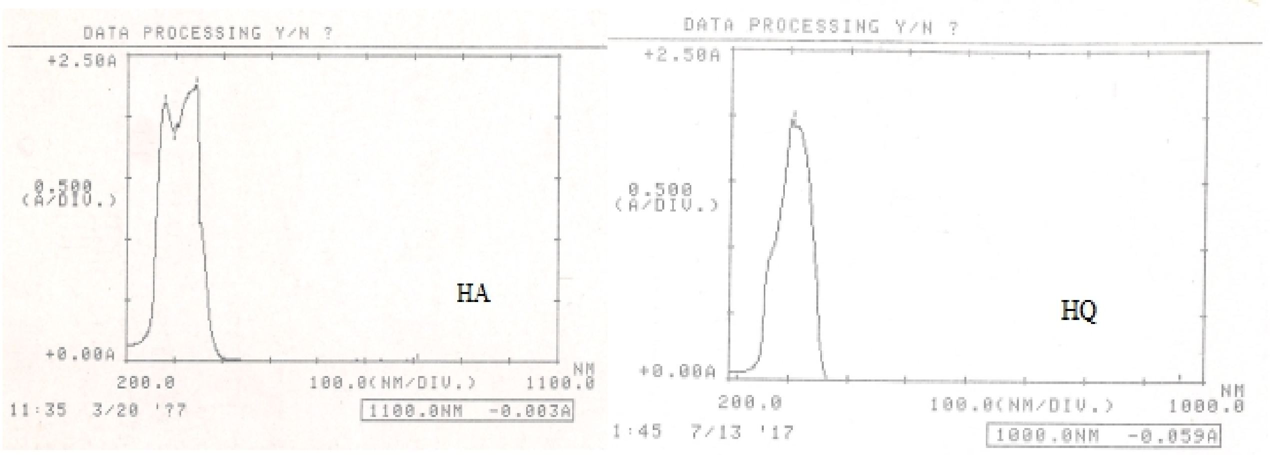


Figure 6. Electronic (HA) and (HQ) spectrum

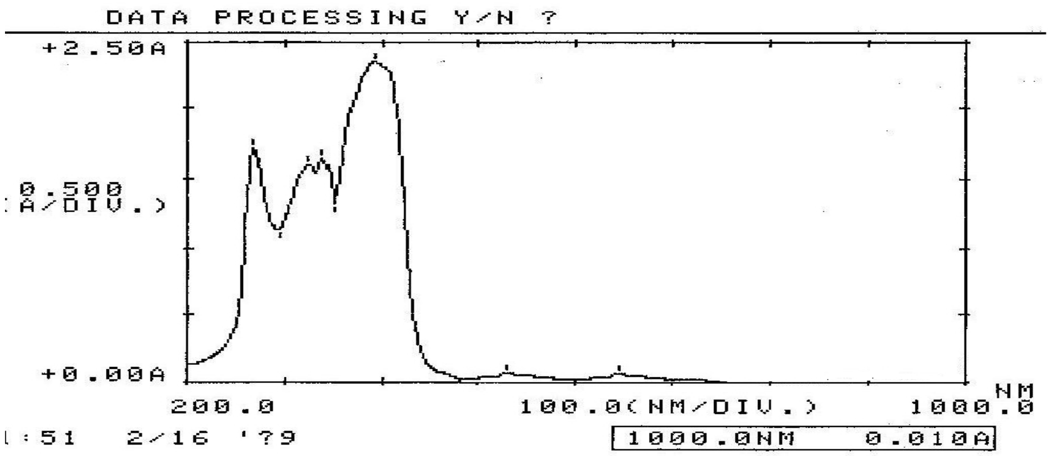


Figure 7. Electronic spectrum of $[Co(A)(Q)(H_2O)_2]$ complex

Thermal analysis complexes

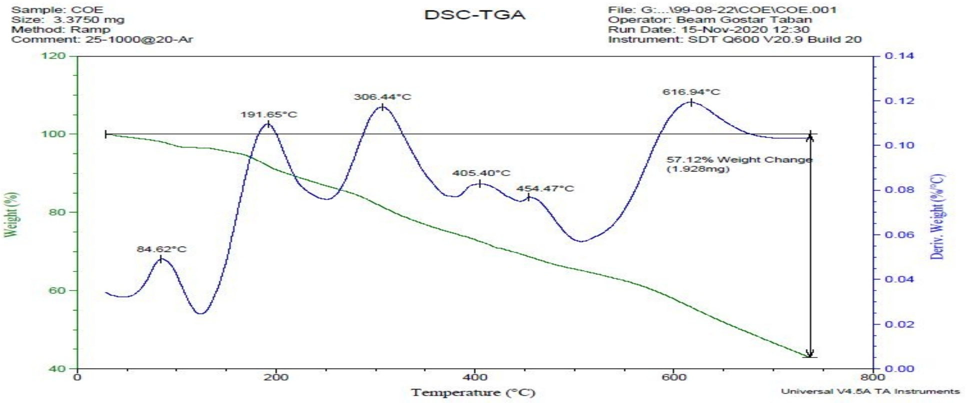
Thermal decomposition of $[Co(A)(Q)(H_2O)_2]$ complex

The thermogram of $[Co(A)(Q)(H_2O)_2]$ is depicted in figure (8), data are listed in table(4). The first step occurred at (28.96-126.72°C) may be attributed to the loss of a molecule of the (H_2O)fragment; (obs.=0.1181 mg, 3.498%; cal=0.0996mg,2.9532%).The second step occurred at (126.72-250°C) indicated the loss of (H_2O_2+CN) fragment;(obs.=0.3229 mg, 9.569%; calc.=0.3322 mg, 9.8442 %).The third step recorded at (250-372.8°C)indicated the loss of (C_6H_6)fragment, (obs.=0.4114 mg, 12.19%; calc.=0.4319 mg, 12.7975%). The four step recorded at (372.8- 442.24°C) indicated the loss of (NO) fragment;(obs.=0.1769mg, 5.242%; calc.=0.1661 mg, 4.9221%).The five step recorded at(442.24 – 734.4°C) indicated the loss of $(C_6H_6+C_6H_6)$ fragment;(obs.=0.8993 mg, 26.65%; calc.=0.8638 mg, 25.5951%).The final residue of the $(C_{15}H_{13}O_2+$ CoO) calc.= 1.6606 mg, 49.205%.The final product is much less than the estimated weight showing the partial sublimation.The DTGA indicated several peaks at 84.62°C,191.65°C,306.44°C,405.40°C,454.47°C and

616.94°C.In the DSC analysis, peaks at 84.62°C,191.65°C,306.44°C,405.40°C,454.47°C and 616.94°C are correlated to exothermic.The exothermic peaks may indicate the combustion of the organic ligand in nitrogen atmosphere[34,35].

Thermal decomposition of $[Cu(A)(Q)(H_2O)_2]$ complex

The thermogram of $[Cu(A)(Q)(H_2O)_2]$ is depicted in figure(9), data are listed in table(4). The first step occurred at (36.37-129.97°C) may be attributed to the loss of a molecule of the (H_2O_2)fragment; (obs.=0.1360 mg, 5.910%; cal=0.127 mg,5.536%).The second step occurred at (129.97-226.64°C) indicated the loss of (H_2O+CN) fragment;(obs.=0.1558 mg, 6.772%; calc.=0.1648 mg, 7.1649%).The third step recorded at (226.64-339.96°C) indicated the loss of $(O_2+C_6H_6)$fragment; (obs.=0.4029 mg, 17.51%; calc.=0.4121 mg, 17.9123 %). The four step recorded at(339.96-683.25°C) indicated the loss of $(NO+C_6H_6+C_6H_6)$ fragment;(obs.=0.7045 mg, 30.62%; calc.=0.6969 mg, 30.288%).The final residue of the $(C_{15}H_{13}+ CuO)$ calc.= 1.021mg, 44.37%.The final product is much less than the estimated weight showing the partial sublimation.The DTGA indicated several peaks at 182.72 and 281.33°C. In the DSC analysis,peaks at 182.72 and 281.33°C are correlated to exothermic.The exothermic peaks may indicate the combustion of the organic ligand in the nitrogen medium [34, 35].



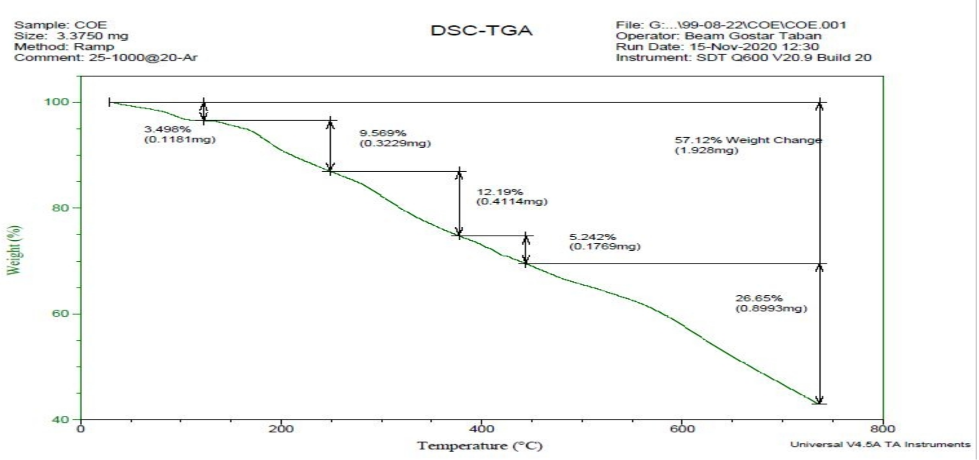


Figure 8. (TG/DTG & DSC) Thermogram of [Co(A)(Q)(H_2O)$_2$] complex

Figure 9. (TG/DTG & DSC) Thermogram of [Cu(A)(Q)(H_2O)$_2$] complex

Table 4. Thermal analysis data of [Co(A)(Q)(H_2O)$_2$]and [Cu(A)(Q)(H_2O)$_2$] complexes

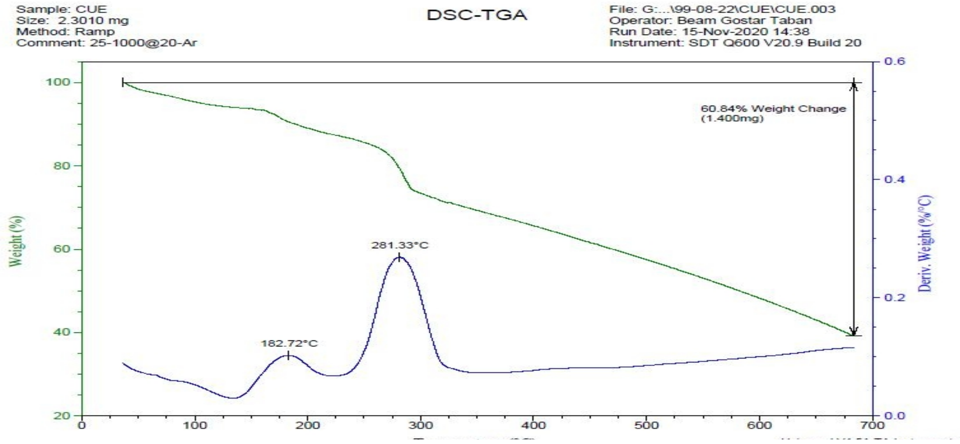
Compound	Stage	Decomposition Temperature Initial-Final (ºC)	Transformation/Intermediate Formed % mass found (calc.)	Nature of DSC peak and Temp. ºC
[Co(A) (Q) (H_2O)$_2$]	1	28.96-126.72	0.1181(0.0996)	84.62 Exo
	2	126.72-250	0.3229(0.3322)	191.65 Exo
	3	250-372.8	0.4114(0.431)	306.44 Exo
	4	372.8-442.2	0.1769(0.1661)	405.40 Exo
	5	442.2-734.4	0.8993(0.8638)	454.47,616.94 Exo
[Cu(A)(Q) (H_2O)$_2$]	1	36.37-129.97	0.1360(0.127)	-
	2	129.97-226.64	0.1558(0.1648)	182.72 EXO
	3	226.64-339.96	0.4029(0.4121)	281.33 Exo
	4	339.96-683.25	0.7045(0.6969)	-

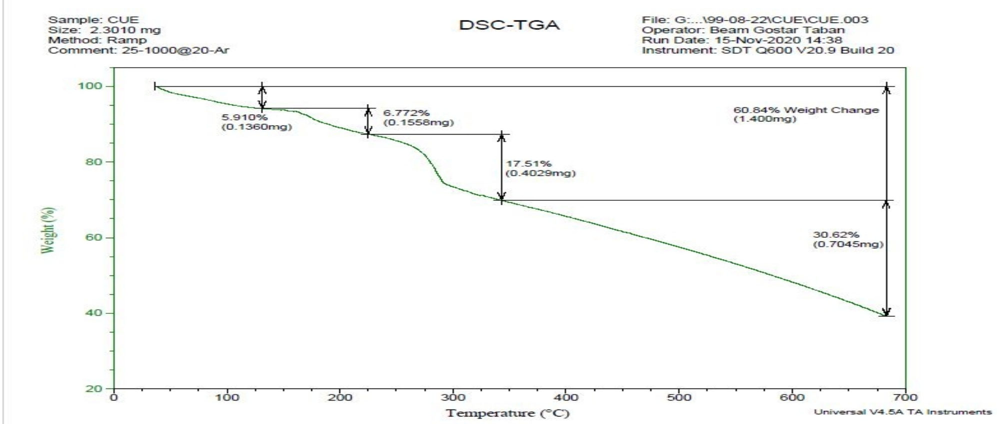
Antibacterial Activity Studies

The results obtained for antibacterial test models studies by agar well–diffusion bioassay revealed biological activities of free ligands in addition to their metal complexes after 24h in table (5), figures (10,11). A comparative study of free ligands in addition to their metal complexes has shown that free ligands (HA) and (HQ) exhibited a lower antibacterial activity than their complexes. All complexes showed higher activity effects against the growth of *Staphylococcus aureus* and *Esherichia Coli*. The [Hg(A)(Q)]complex has shown positive effects against the organisms exhibiting moderate to high activities and the inhibition zone (38-40mm) [36,37]. The increase in the metal complexes' inhibition activity may be explained based on Tweedy's theory of chelation [38]. In the metal complexes, on the chelation the metal ion polarity can be decreased to a higher level, as a result of the overlapping of ligands partial and orbital sharing of positive charges of metal ions with the donor groups [36,39].

Table 5. Diameter of the Inhibition Circle in (mm) for Bacteria after 24hr. Incubation at 37 ^{0}C for the compounds

No.	Compounds	Gram negative (G+)	Gram negative(G-)
		***Staphylococcus aureus*(G+)**	***Esherichia Coli* (G-)**
1	(HA)	10	14
2	(HQ)	18	15
3	[Mn(A)(Q)]	26	17





4	$[Co(A)(Q)(H_2O)_2]$	26	23
5	$[Cu(A)(Q)(H_2O)_2]$	34	25
6	$[Zn(A)(Q)]$	29	26
7	$[Cd(A)(Q)]$	32	29
8	$[Hg(A)(Q)]$	38	40
C	DMSO	-	-

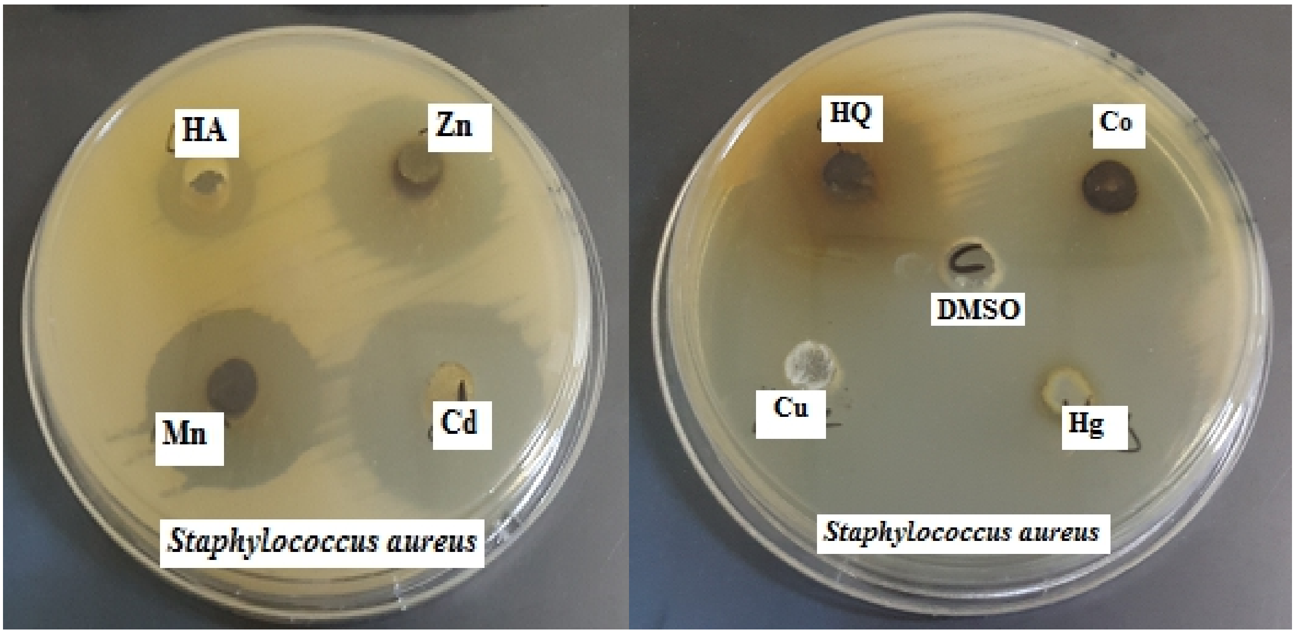


Figure 10. The effects of ligands and their complexes on *S. aureus*

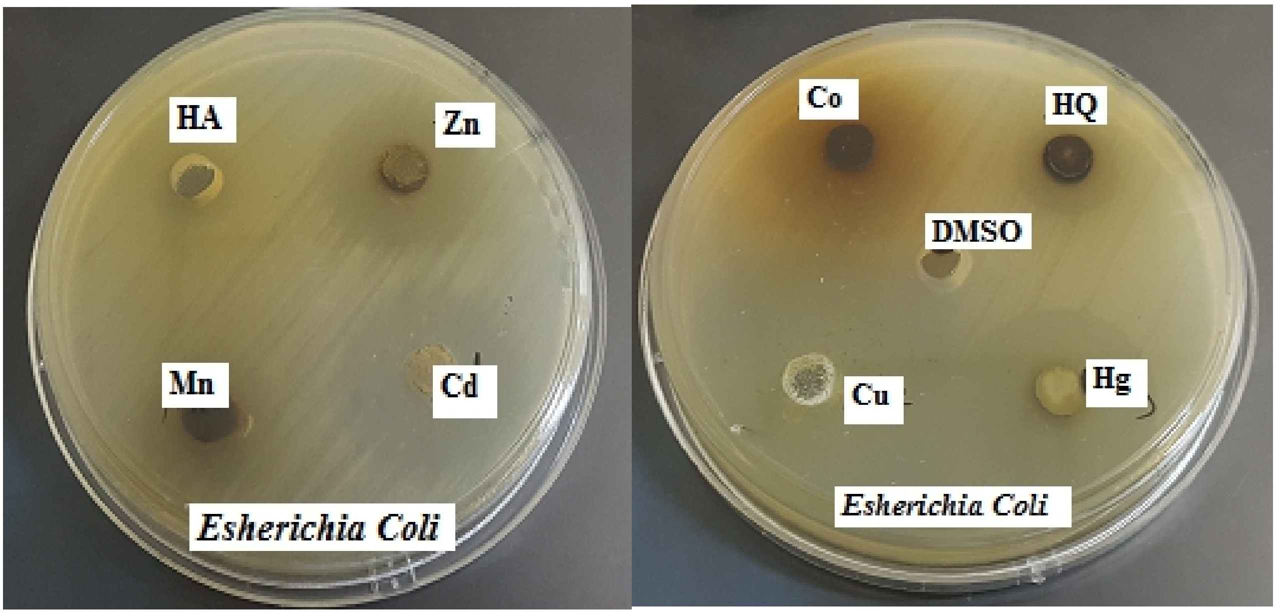


Figure 11. The effect of ligands and their complexes on *E. coli*

CONCLUSION

Series of new mixed ligand complexes have been produced with 4,4'-((naphthalen-1-ylimino)methylene)dibenzene-1,3-diol as a primary ligand (HA), 8HQ as a secondary ligand (HQ) with Mn(II), Co(II) , Cu(II), Zn(II), Cd(II), and Hg(II) in mole ratio (1:1:1) of mixed ligands complexes as two formulas [M(A)(Q)] which have tetrahedral geometry and $[M(A)(Q)(H_2O)_2]$ were octahedral geometry . The complexes of the mixed ligand may be a synthetic challenge for tuning metal complexes' characteristics. The biological data has shown that the complexes became of a higher activity towards those tested bacteria in comparison to free ligands.

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