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Synthesis, Spectroscopic and Antimicrobial Assessments of Cu(II), Co(II), Ni(II) and Pb(II) Clioquinol Complexes

Hammad Fetooh

Department of Chemistry, Faculty of Science, Zagazig University, Egypt

OUR goal in this article is to synthesize of four novel clioquinol (Clio) drug complexes for the Co(II), Ni(II), Cu(II) in addition to Pb(II) . On the basis of spectroscopic, magnetic, conductance and thermal studies, the complexes have been characterized. Free ligand acts as abidentate chelate with metal ions through its two atoms Oxygen in addition to nitrogen. Structural formulas for Clio complexes have chemical formulas $[Co(Clio)_2(H_2O)_2].2H_2O$, $[Ni(Clio)_2(H_2O)_2].H_2O$, $[Cu(Clio)_2(H_2O)_2].H_2O$ in addition to $[Pb(Clio)_2].2H_2O$. The thermal decomposition of all complexes contains metal oxides as a residue in its final degradation steps. The antimicrobial activities of the complexes are in a good assessment and the synthesized complexes have a higher activity with lipophilic nature against bacteria and fungi.

Keywords: Clioquinol; FTIR; Thermal analyses; Electronic spectra; Antimicrobial activity.

Introduction

Cliquinol (5-chloro-7-iodo-8-hydroxy quinoline; Fig. 1), belongs to the quinoline class of compounds, belonging to the family of drugs called anti-infective. In the period from 1950s to 1970s, antibiotics as clioquinol were used [1,2]. In treatment of amoebic dysentery and skin infections,an antibiotic as clioquinol was widely used [3]. For humans, clioquinol has been used and observed that the cause for an epidemic of a rare neurological disease (subacutemyelopticneutropaathy (SMON) in Japan and banned in various countries [4,5]. With respect to Alzheimer's disease, clioquinol has been managed for clinical trials [6,7].

Clioquinol is suitable for forming complexes that are stable with Cu(II), as clioquinol is aphenolic compound and lipophilic [4]. The clioquinol complexes of Cu(II) and Zn(II) are known for their biological activities which are in accordance of protein aggregation and degeneration process in the brain [4], also these complexes

have been screened as an antimicrobial agent [8-10]. Halogenated derivatives of 8-hydroxy quinoline have enough used in the generation of useful therapeutic complexes of Ga(III) [11-19]. The targeted proper to obtain deep studying for structural, magnetic, spectral properties such as IR , H[1]-NMR, Electronic absorption and microbial activities for Cu(II), Co(II), Ni(II), and Pb(II) complexes of clioquinol in comparison with it is reported . The present study is dealing with investigation metal-clioquinol complexes by thermal and spectral techniques.
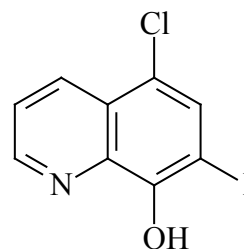

Fig. 1. Structure of clioquinol free ligand drug

Experimental

Chemicals

The chemicals with the purest laboratory degree were received from Merck chemical company as $Co(OAc)_2.4H_2O$, $Cu(OAc)_2.H_2O$, $NiCl_2.6H_2O$ and $Pb(OAc)_2.3H_2O$. Clioquinol presented from Egyptian International Pharmaceutical Industrial Company (EIPICO).

Preparation of clioquinolcomplexes

Co(II), Cu(II), Ni(II), and Pb(II) complexes were prepared upon the reaction mixtures of $Co(OAc)_2.4H_2O$, $Cu(OAc)_2.H_2O$, $NiCl_2.6H_2O$, and $Pb(OAc)_2.3H_2O$ salts of (1 mmole) in 20 mL dist. H_2O to dissolved clioquinol in 20 mL of CH_3OH with molar ratio as (1:2) (metal: ligand). Using 5% alcoholic ammonia solution, the pH of each solution was adjusted at pH = 7. At room temperature, the forming solution was stirred, refluxed on a hot plate for 60-70°C at 2 hrs and left slowly to evaporate. Using hot water and drying at 70°C, The resultant precipitates were filtered off and washed several times, respectively.

Instruments

Using a Perkin-Elmer CHN2400, the CHN contents were determined. The contents of metals were calculated gravimetrically due to convert of the compounds into their corresponding oxides till constant weight. The rest of complexes after ignition was clearly weighed as metal oxides. Using Jenway 4010 conductivity meter, molar conductivity of freshly prepared 10^{-3} M in DMSO solution of the complexes was carried out. Using Bruker FT-IR spectrophotometer (4000-400 cm^{-1}), IR spectra were recorded in KBr pellets. Using Perkin Elmer Lambda 4B spectrophotometer, the UV-Vis spectrum of complexes was measured in DMSO solvent at concentration of 10^{-3} M in the range of 190-900 nm. At room temperature using Gouy's method, mass susceptibility (Xg) of complexes was measured by magnetic susceptibility balance of Sherwood models. Using the following equations, the effective magnetic moment (μ_{eff}) value was obtained.

$$Xg = \frac{C_{Bal}L(R-Ro)}{10^9 M} \quad (1)$$

Where Ro = Reading for an empty tube, L = Sample length in cm, M = Sample Mass in g, R

= Reading of tube and sample and C_{Bal} = Balance calibration constant (2.086).

$$X_M = Xg*M.Wt \quad (2)$$

Using pascal's constant, the value of X_M that calculated from equation (2) are corrected for the diamagnetism of the ligand and applied in Curie's equation (3).

$$\mu_{eff} = 2.84 \sqrt{X_M X_T} \quad (3)$$

Where, T (k) = t (c°) + 273

On Varian Gemini 300 MHz spectrophotometer, the ^{1}HNMR spectra of free clioquinol ligand and its complexes were recorded using TMS an internal reference and DMSO-d6 as solvent. using Shimadzu TGA-50H thermal analyzers, both Thermogravimetric analyses TG and DTG were carried out at temperature ranged from 25 to 800°C, rate of flow at 30 mL.min^{-1} and heating rate of 10°C min^{-1} under nitrogen atmosphere.

Microbiological investigation

The examined fungi and bacteria were cultivated at tubes with Dox's broth (DB) and nutrient broth (NB), respectively.

The cultivated (DB) for fungi and (NB) for bacteria of (1mL) were homogenously mixed in the tubes with 9 mL of melted nutrient agar (NA) for bacteria and (DA) for fungi at 45°C. Then suspension was homogenously poured to petri dishes. In the cool medium, holes with 0.5 cm diameter were done and $2x10^{-3}$ dm^3 of the examined compounds applied using microipeptte, in an incubation at 24 hrs in thermostat from 25 to 27°C. The diameter of inhibition zone was expressed and measured in cm. The antimicrobial effects of examined compounds were screened versus *Bacillus Subtilis* like (Gram +ve) bacteria, *EscherichiaColi* like (Gram –ve) bacteria in addition to some kinds of fungi like *Aspergillus Niger* and *Aspergillus Flavus*.

Results and Discussion
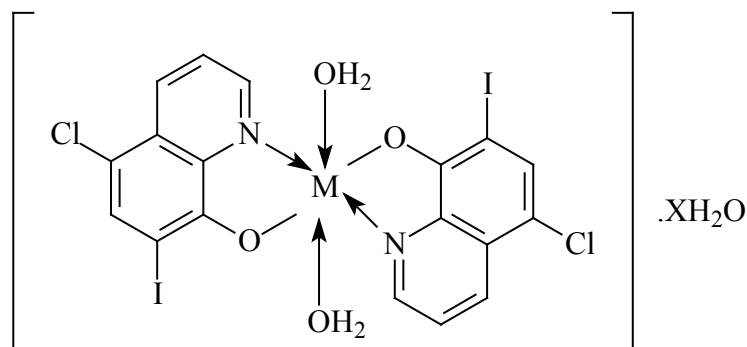
Physicoanalytical properties

The physicoanalytical data of the free Clioquinol ligand and its Co(II), Ni(II), Cu(II) and Pb(II) complexes are listed in Table 1. The complexes of clioquinol have higher melting points, so, they

are thermally stable in air. These synthesized complexesare insoluble in H_2O, most organic solvents except for DMF, DMSO and concentrated acids are soluble. The analyses of elements of clioquinolcomplexes show molar ratios are (1:2) (metal: ligand) for all divalent state metals. At room temperature, The measured magnetic moment for Co(II), Ni(II), and Cu(II) complexes of clioquinol was paramagnetic in nature while, Pb(II) complex of clioquinol possessesa diamagnetic nature.Values of molar conductance for all clioquinol complexes in the range of (12- 19 $\Omega^{-1}.cm^2.mol^{-1}$), were naturally seemed as non-electrolytes [20] . The elemental analyses data of the proposed complexes are in a well matching with these results (Fig. 2).

TABLE 1. Elemental analyses and physical data of clioquinol complexes

Molecular formula	M.M (g/mol)	Λ_M ($\Omega^{-1}.cm^2.mol^{-1}$)	Elemental analysis, % F% (Calculated)			
			Carbon	Hydrogen	Nitrogen	Metal
[CO(Clio)$_2$(H$_2$O)$_2$].2H$_2$O	740	17	29.16	1.69	3.61	8.28
			(29.19)	(2.16)	(3.78)	(7.97)
[Ni(Clio)$_2$(H$_2$O)$_2$].H$_2$O	722	14	29.85	1.48	3.78	8.21
			(29.92)	(1.94)	(3.88)	(8.17)
[Cu(Clio)$_2$(H$_2$O)$_2$].H$_2$O	726.5	19	29.63	1.69	3.51	8.92
			(29.73)	(1.93)	(3.85)	(8.74)
[Pb(Clio)$_2$].2H$_2$O	851	12	25.94	1.47	3.13	24.50
			(25.40)	(1.40)	(3.28)	(24.30)

Where, M = Cu(II), Ni(II) and Co(II) and X = 1 and 2, respectively.
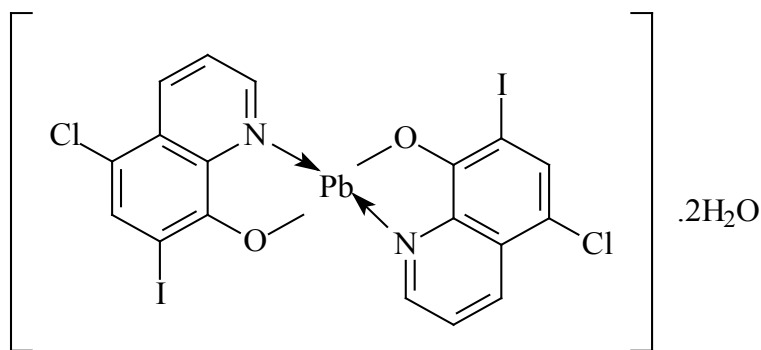
Fig. 2. Mode of chelation of clioquinol complexes.

Infrared spectra

In Figs.3a-d, the spectra of IR for all Clioquinol complexes within the spectral range from 4000 to 400 cm^{-1} are shown andin Table 2, the proposed assignments are presented. The summarized infrared results are shown as follows:

i. In the range of 3400-3785 cm^{-1}, the IR spectra of complexes of Co(II), Ni(II), Cu(II), and Pb(II) clarify the asymmetric stretching vibrations ν_{as}(O-H) of water molecules due to broadening, while the complementary symmetric vibrations can be assigned to the weak intensity band around ~ 3150 cm^{-1}. The appearance of two band vibrations for H$_2$O molecules gives an indication about the participation of coordinated and uncoordinated H$_2$O molecules [21-26].

ii. In the IR spectrum of free clioquinol ligand, the characteristic strong and broad stretching band, ν(OH) that appeared at 3065 cm^{-1} are disappeared after complexation. Only a weak band remains in this region, which can be assigned to ν(CH) of aromatic rings [23-26].

iii. At deprotanation, the band which can be assigned to the ν(C-O) vibration shifted to somewhat greater values in the complexes from 1103 to 1273 cm^{-1}. Also, in the IR spectrum of the free ligand, the deformation mode as out-of plane of ν(C-OH) located at 496 cm^{-1}, is moved to lower values in the complexes, as well as the expected in plane deformational mode that found within the CH in-plane vibrations [26].

iv. Stretching vibrations of ν(C=C) bands, are located at similar values as in the ligand alone (1540-1550 cm^{-1}), subsequently, on the contrast, the ν(C=N) Stretching bands are strongly influenced for coordination and appeared at 1660-1709 cm^{-1} [25].

v. The IR peaks at 810-899 and 721-754 cm^{-1}, ν(OH) of coordinated water, is an indication for the attachment in the water molecules with the metal ions. New peaks are exhibited in the spectra of the complexes at the region 656-560 and 506-405 cm^{-1}, that may be assigned to ν(M-O) and ν(M-N) stretching [25,26], respectively, as referred in Table 2.

TABLE 2. IR frequencies (4000-400 cm^{-1}) of Clioquinol complexes

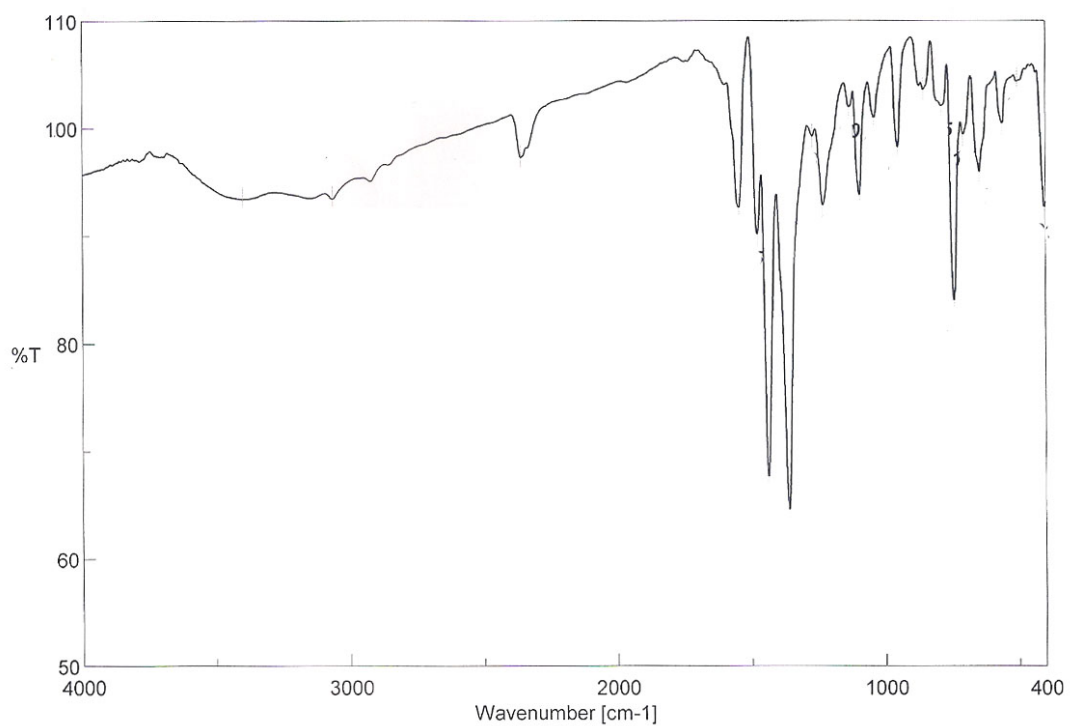| Complex	ν(OH); H$_2$O	ν(C-H); aromatic	ν(C=N)	ν(C=C)	ν(C-O); phenyl	ν(M-O)	ν(M-N)
Co(II)	3400, 3780	3063	1664	1550	1240,1140	581	436
Ni(II)	3398, 3781	3066	1709	1547	1273,1239,1197	562	497
Cu(II)	3400, 3782	3065	1660	1547	1273,1234,1135	561,506	405
Pb(II)	3783, 3440	3064	1662	1554	1260,1195	569,502	432
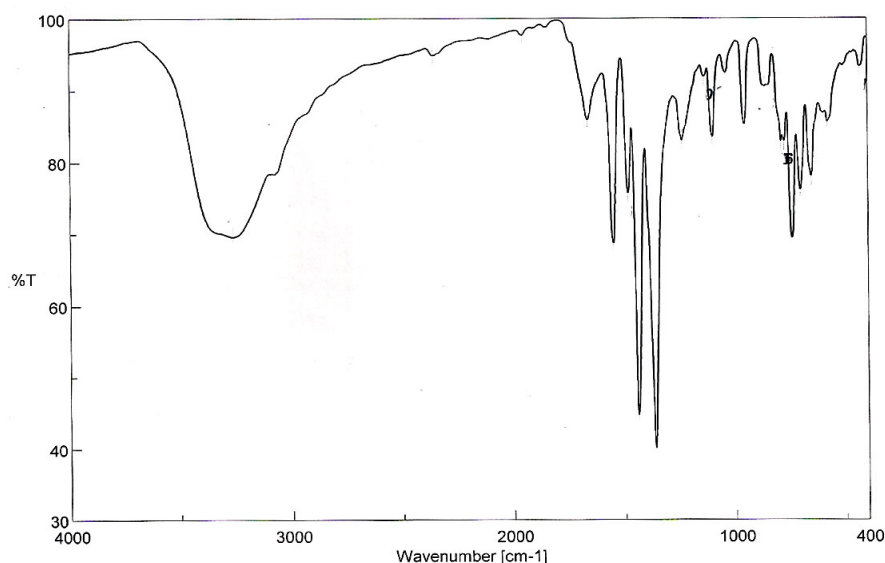
Fig. 3a. IR spectrum of Co(II) clioquinol complex
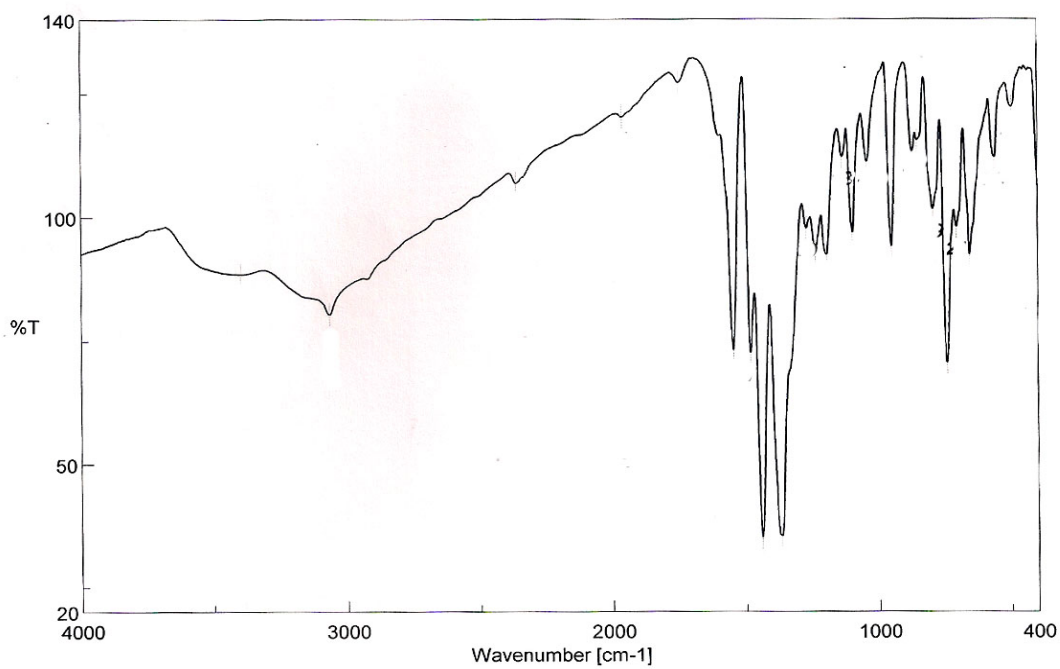
Fig. 3b.IR spectrum of Ni(II) clioquinol complex

Fig. 3c.IR spectrum of Cu(II) clioquinol complex
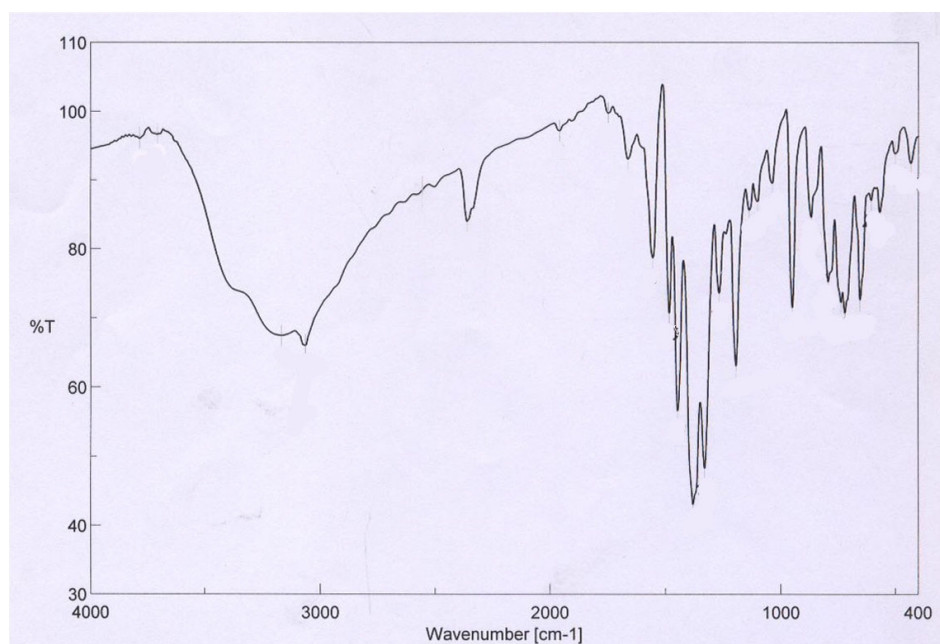
Fig. 3d.IR spectrum of Pb(II) clioquinol complex.

Magnetic and electronic absorption spectra

In the free Clioquinol ligand, two characteristic absorption bands are exhibited. The band firstly at 300 nm is due to π-π* intra ligand electronic transition for the aromatic ring and the other band noticed at 390 nm is due to n-π* electronic transition. In the spectra of the clioquinol complexes, the observed bands are attributed to hypsochromic shift (blue effect), which donate clear suggestion about the deprotonated ligand, the unshared pair of electrons in nitrogen and phenoxy moiety that shared in the coordination mode.

The electronic spectrum of the copper (II) complex showed mainly transition bands at 440 nm ascribe to $^2E_g \rightarrow {^2T_{2g}}$ transition in distorted octahedral geometry [27,28]. The other detectable band at 372 nm was assigned to L→M charge transfer. The found value of the magnetic moment of Cu(II) complex was 1.74 B.M., which supported the octahedral feature [27,28]. The magnetic moment of Co(II) complex was found at 3.80 B.M. at room temperature which supported the octahedral geometry. There are two detectable bands were observed at 450 nm and 355 nm due to $^4T_{1g} \rightarrow {^4A_{2g}}$ and $^4T_{1g} \rightarrow {^4T_{1g}}(P)$ transition, respectively. The nickel (II) complex that has an octahedral geometry exhibit three bands which are assigned to $^3A_{2g} \rightarrow {^3T_{2g}}$ (F), (v1); $^3A_{2g} \rightarrow {^3T_{1g}}$ (F), (v2) and $^3A_{2g} \rightarrow {^3T_{2g}}$ (P), (v3) transition, respectively. The $^3A_{2g} \rightarrow {^3T_{2g}}$ (P), (v3) transition band is occurring within the 360 nm. The $^3A_{2g} \rightarrow {^3T_{2g}}$ (F), (v1) and $^3A_{2g} \rightarrow {^3T_{1g}}$ (F), (v2) transition bands are observed within the 530-780

nm region [27].

Thermal analyses

Within the corresponding ranges of temperature, losses of weight for each complex were calculated; the calculated and observed results are recorded in Table 3 and shown in Figs.4a-d.

The thermal decomposition for Co(II) complex takes place in three stages. At the range from 60 to180°C, decomposition step firstly occurs and corresponds to removal molecules of two uncoordinated water due to the observed loss of weight = 3.96% and calculated loss of weight = 4.86%. At the range from 260 to 406°C, the decomposition step secondly lies that corresponds loss for $2H_2O$, $0.5\ Cl_2$ and $0.5\ I_2$ with a weight loss (obs. = 27.74%, calc. = 26.83%). The third step is exhibited at 400-675°C, which is accompanied by degradation for Clioquinol moiety of remained 3C atoms with loss of weight = 52.57% and the corresponding value that calculated = 53.30%. The final product that stably stills at 800°C is (CoO + 3C).

In four stages, Ni(II) complex is broken down. Decomposition step is firstly appeared from 90 to175°C with accompanied for H_2O loss and represented loss of weight of observed value = 3.39% and calculated value = 2.50%. At the range from coordinated of loss weight (obs. = 5.37%, calc. = 5.00%). The third step is occurring at 290-

415°C, The stage secondly falls and corresponds to $2H_2O$ loss as coordinated of loss weight (obs. = 5.37%, calc. = 5.00%). The third step is occurring at 290-415°C and corresponding to the removal of $(Cl_2 + 0.5\ I_2)$ and the represented loss of weight = 26.66% and calculated = 27.40%. at the temperature range from 415 to 655°C, stage finally occurs and assigns the loss of organic moiety as $C_{18}H_8IN_2O$ of observed loss weight = 54.14% and calculated value = 54.73%). At 800°C, NiO is finally resulted as product.

The thermal degradation of Cu(II) complex takes place at three stages. Within the range from 100-210°C, decomposition stage firstly occurs, it represents evolution for one molecule of uncoordinated H_2O and observed loss of weight with 2.50%, calculated = 2.48%. Stage secondly ranged at 210-370°C, which assigned to loss of $(2H_2O + 0.5\ I_2)$ with observed loss of weight of 22.27%, calc. = 22.42%). At the range from 370 to 630°C, stage finally occurs, corresponds to loss with organic moiety as $C_{12}H_8Cl_2N_2IO$ of

loss weight of 53.95% and (calculated = 54.21%). CuO polluted with six carbon atoms and finally resulted as product at 800°C.

In five stages, Pb(II) complex breaks down. Decomposition stage is firstly appeared in 96-190°C of corresponded loss with $(H_2O + I_2 + N_2)$ and represented loss of weight (observed = 21.38%, calculated = 21.18%). stage is secondly ranged at 190-360°C, which assigned to loss of $2HI$, N_2 and $2Cl_2$ and represented loss of weight (observed = 29.83%, calculated = 28.38%). Third stage is occurred in 360-510°C, which corresponded removal for $C_{12}H_6O$ and represented loss of weight (observed = 12.01%, calculated = 11.06%). Fourth stage occurs in range from 510 to 600°C, assigns for organic moiety as $C_{21}H_7O$ of loss of weight (observed = 20.22%, calculated = 18.32%). Stage is finally ranging at 600-700°C with corresponding of C_3H_3O loss of weight (observed = 3.62%, calculated = 3.66%). Finally, at 800°C, the produced PbO is obtained.

TABLE 3. Thermo gravimetric analyses for complexes of clioquinol

| Compound	stages	DTG$_{peak}$ /(°C)	decomposition products	Loss of Weight, % F (calc. %)
Co(II)	1st	140	$2H_2O$	3.96 (4.86)
	2nd	340	$2H_2O+0.5Cl_2+0.5I_2$	27.74 (26.83)
	3rd	560	$C_{15}H_8ClIN_2O$	52.71 (53.30)
	Residue		CoO+3C	-
Ni(II)	1st	140	H_2O	3.39 (2.50)
	2nd	230	$2H_2O$	5.37 (5.00)
	3rd	330,350	$Cl_2+0.5I_2$	26.66 (27.40)
	4th	500	$C_{18}H_8IN_2O$	54.14 (54.73)
	Residue		NiO	-
Cu(II)	1st	140	H_2O	2.50 (2.48)
	2nd	295	$2H_2O+0.5I_2$	22.27 (22.42)
	3rd	465	$C_{12}H_8Cl_2N_2IO$	53.95 (54.21)
	Residue		CuO+6C	-
Pb(II)	1st	170	$2H_2O+I_2+N_2$	21.38 (21.18)
	2nd	310	$2HI+N_2+2Cl_2$	29.83 (28.38)
	3rd	497	$C_{12}H_6O$	12.01 (11.06)
	4th	550	$C_{21}H_7O$	20.22 (18.32)
	5th	650	C_3H_3O	3.62 (3.66)
	Residue		Pbo	-
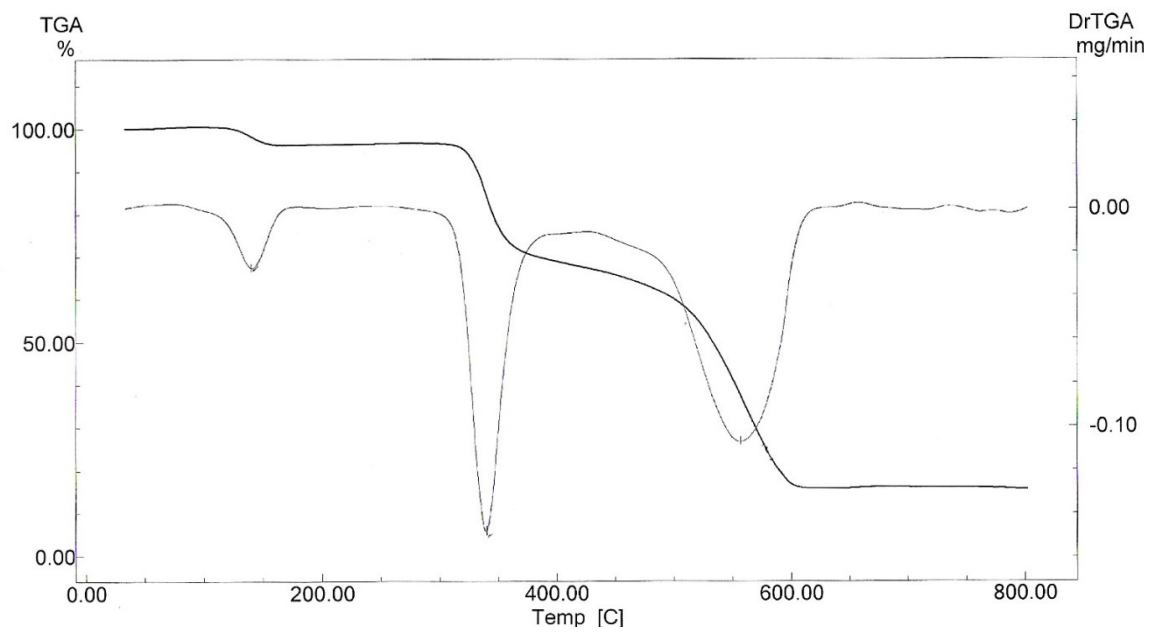
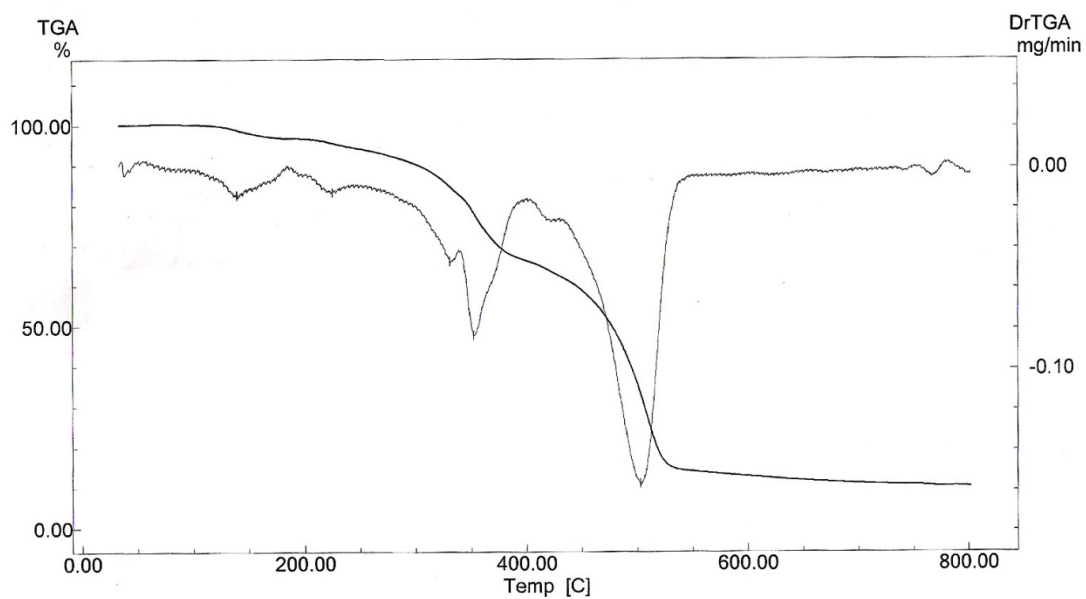**Fig. 4a.TG/DTG curve of Co(II) clioquinol complex.**

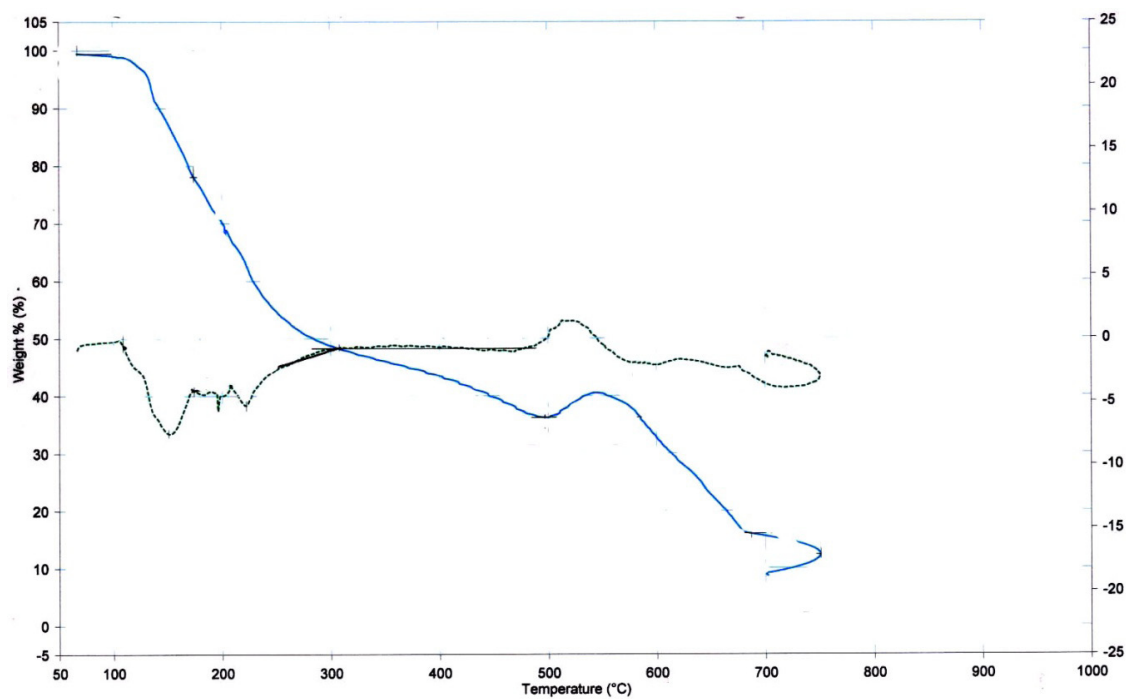**Fig. 4b.TG/DTG curve of Ni(II) clioquinol complex.**

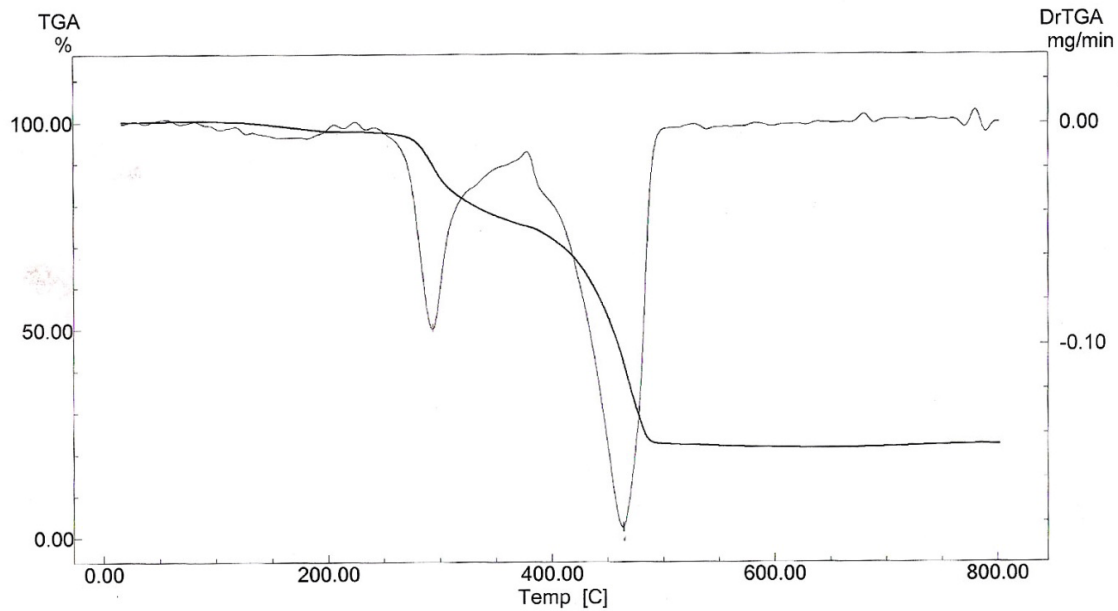**Fig. 4c.TG/DTG curve of Cu(II) clioquinol complex.**

Fig. 4d.TG/DTG curve of Pb(II) clioquinol complex.

1H-NMR spectrum

By 1H-NMR spectrum for Pb(II) complex, the assignments of chelation modes were further supported. Hence, 1H-NMR spectrum of Pb(II) complex (Fig. 5) in comparison to the spectrum for clioquinol free ligand clarify the potential site of complexation of clioquinol ligand takes place via the nitrogen atom of Quinoline-moiety, (OH) moiety of phenolic-group due to disappearance

for proton signal which appears at 5.00 ppm in the free ligand. The signals of aromatic protons at 6.00-8.00 ppm may be noticed due to different chemical environments of decreased intensities. at $\delta=3.35$ ppm, spectrum of 1H-NMR for Pb(II) complex clarify this peak that unnoticed for spectrum of free ligand ,indicating the presence of protons for molecules of water in accordance with formula of complex as $[pb(Clio)_2].2H_2O$.
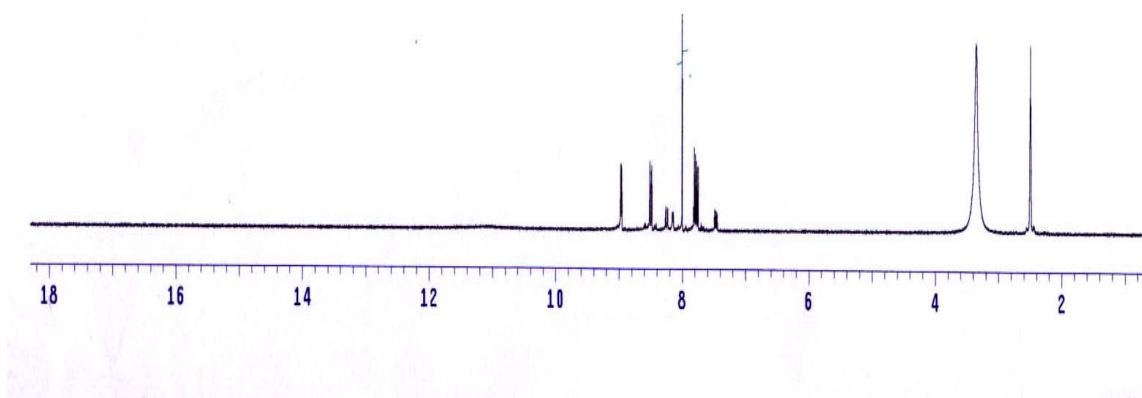
Fig. 5.1H-NMR spectrum of Pb(II) clioquinol complex.

Antimicrobial investigation

The antimicrobial and antifungal activities of clioquinol complex Fig. 6 and Table 4 screened versus gram +ve as *B. Subtilis* and (gram –ve) as *E. coli* in addition to antifungal (*A. Niger, A. Flavus*). Antimicrobial and antifungal effects show that, Cu(II), Ni(II) , and Co(II) complexes have high activities versus bacteria in addition to fungi, on the other hand ,these mentioned complexes have no activity towards (gram –ve)

as *E. coli* . But, in case of Pb(II) complex, it is observable that this complex possesses the highest activity for all different kinds of both bacteria and fungi. So, it is clear that the complexation with metal ion increased the sensitivity factor of ligand versus fungi in addition to bacteria, as; chelation improved and enhanced activity for complexes [29].

TABLE 4. Diameter of inhibition zone (cm /mg sample) for complexes of Clioquinol versus some kinds for bacteria with fungi.

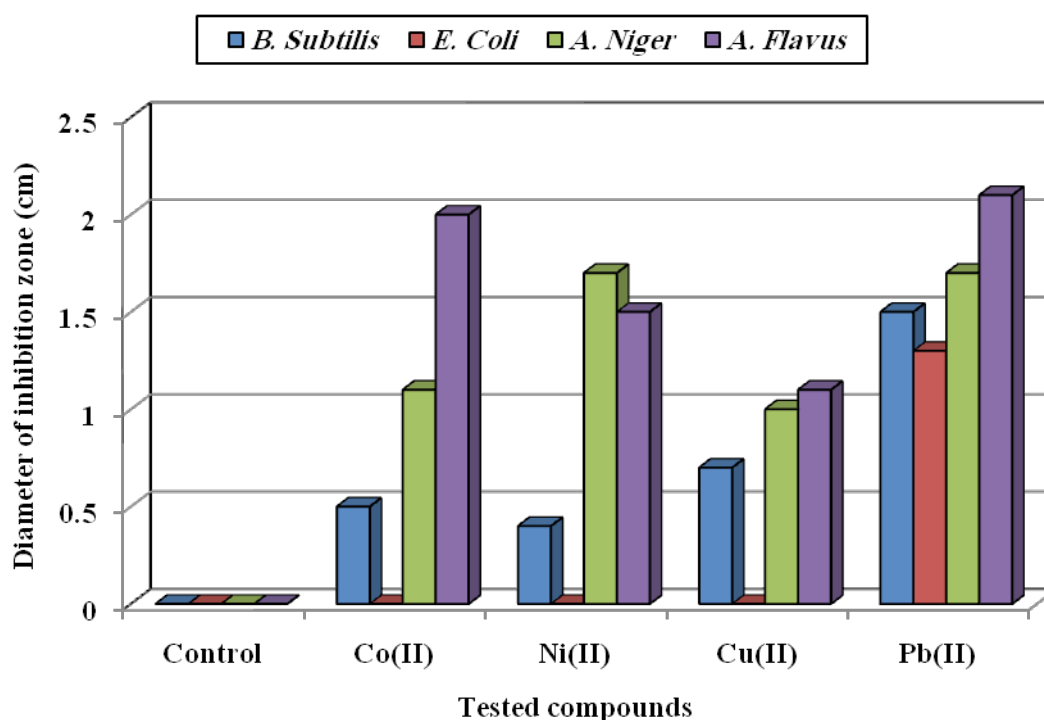| Species	Inhibition zone diameter (cm.mg^{-1})			
	B. Subtilis	*E. Coli*	*A. Niger*	*A. Flavus*
Reference DMF	0	0	0	0
Co(II) complex	0.5	0	1.1	2
Ni(II) complex	0.4	0	1.7	1.5
Cu(II) complex	0.7	0	1	1.1
Pb(II) complex	1.5	1.3	1.7	2.1

Fig. 6. Statistical representation for biological activity of clioquinol complexes.

Conclusion

Four novel clioquinol (Clio) drug complexes for the Co(II), Ni(II), Cu(II) in addition to Pb(II) were synthesized and in vitro evaluated for antimicrobial activity. On the basis of magnetic, spectral properties such as IR, ^{1}H-NMR, Electronic absorption, it is observable that the potential site of complexation of clioquinol ligand as bidentate chelate takes place via the nitrogen atom of Quinoline-moiety and (OH) group of phenolic-moiety due to disappearance for proton signal which appears at 5.00 ppm in the free ligand**.** Also**,** octahedral geometries are proposed for all clioquinol complexes except for lead(II)complex exhibited in tetrahedral structure.It is clear that the complexation with metal ions increased the sensitivity factor of ligand versus fungi in addition to bacteria, so, chelation improved and enhanced activity for complexes**.**

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