

Synthesis, Characterization, Thermal and Antibacterial Activity Study of Some Transition Metal Ions Mixed Ligand Complexes Using N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amine and Ciprofloxacin Ligands

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Abstract : This paper describes the preparation of new six metal-ion complexes of the ligand ciprofloxacin (L_1) and N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amine (L_2) with the metal ions Cr^{III} , Mn^{II} , Fe^{III} , Co^{II} , Ni^{II} and Cu^{II} which were prepared in alcoholic medium. Bidentate ligand L_2 = N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amine was prepared by the reeaction of phenanthren-1-amine with 4-chlorobenzaldehyde, in presence of KCN. The metal-ion complexes were prepared in absolute C_2H_5OH with stirring and characterized by the elemental micro analyses (CHN), chloride content, FT-IR, UV-visible spectroscopy and magnetic measurements, 1H -NMR, ^{13}C -NMR spectrae, Thermal Gravimetric Analysis (TGA), as well as molar conductivity. According to the obtained data the possible shapes of the compponds were recommended as octahedral. a number of metal-ion complexes were establish to be weak electrolyes, otheres were set up as nonelectroly.

Keywords : quinolones (ciprofloxacin), N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amine, metal ions.

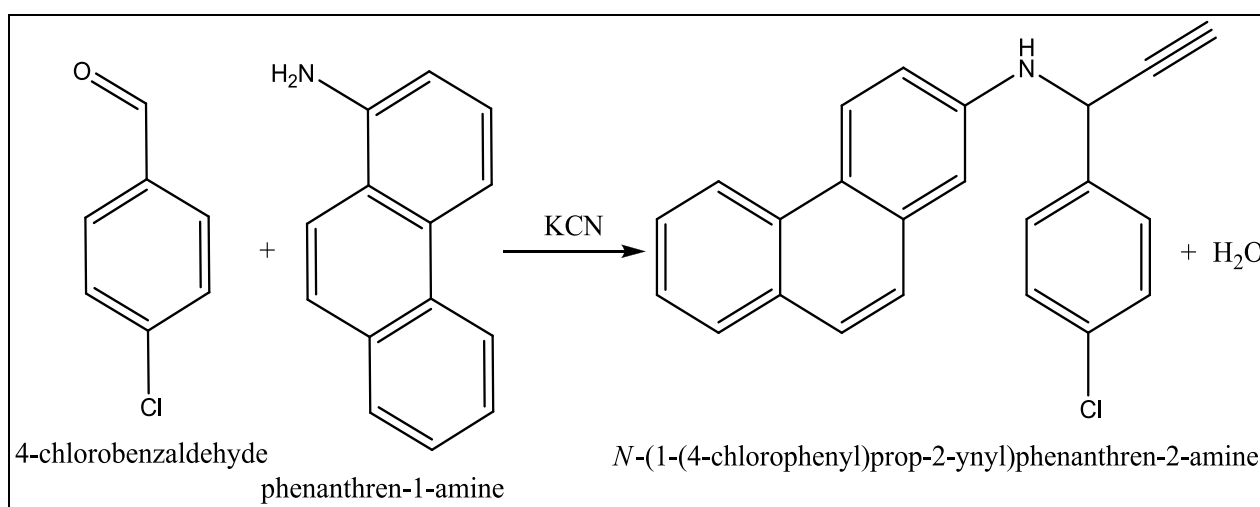
1. Introduction

The main quinolone nucleus is a nitrogen-containing, 8-membered heterocyclic aromatic quinolone ring. Ciprofloxacin is very active against members of the family *Enterobacteriaceae* and other Gram-negative organisms, such as *P. aeruginosa*. Ciprofloxacin possesses a broad spectrum of antimicrobial activity, which includes aerobic Gram-positive and Gram-negative organisms. It has less significant activity against *staphylococci* and borderline or poor activity against, *streptococci*, *anaerobes* and *enterococci*. Methicillin-sensitive and resistant strains of *S. aureus* are usually susceptible to ciprofloxacin.¹ The utility of quinolone derivatives in areas of medication, food, catalyst, dye, materials, efineries and electronics is well-known. As a result the synthesis of quinolone core and its derivatives have been an attractive goal for the synthetic organic chemist. Quinolones form metal complexes due to their capacity to bind metal ions.² In their metal-ion complexes, the quinolones can act as bidentate ligand, as unidentate ligand and as bridging ligand. Frequently, the quinolones are coordinated in a bidentate behavior, through one of the oxygen atoms of deprotonated carboxylic group and the ring carbonyl oxygen atom. The standard term "quinolonee antibiotics" refers to a group of synthetic antibiotics with bactericidal effects, the first compound of the series, was introduced in therapy in the 1960s³ The clinical use of nalidixic acid was narrow by its narrow band of activity. Several modifications were made on the basis nucleus in order to enlarge the antibacterial spectrum and to improve the pharmacokinetics properties, two of these considered as being major: introduction of a piperazine moiety or another N-heterocyclic in the position7 and introduction of a fluoride atom at the position6⁴. The new 4-quinolones, fluoro quinolones, have been exposed starting in the 1980s.⁵ The bactericidal effect of fluoro

quinolones results from induced bacterial apoptosis.¹ With the purpose of exert their action, it has been proposed that fluoro quinolones bind to a specific target site on bacterial DNA.^{6,7}

2. Preparation the Ligand

By changing the primary aromatic amine (phenanthren-1-amine) and (4-chloro benzaldehyde) the ligand (L₂) was prepared by a previously reported method.⁸ Potassium cyanide (0.13gm, 2.0mmol) was dissolve in (0.004L) of distilled water and cooled below 5°C. To this solution, 4-chloro benzaldehyde (0.281gm, 2.0mmol) in (30mL of 95% C₂H₅OH) was added. The mixture was stirred maintaining temperature below 5°C. Glacial CH₃COOH (0.12gm, 2.0mmol) was added with constant stirring, this was followed by the addition of phenanthren-1-amine (0.386gm, 2.0mmol) in (10mL of 95% C₂H₅OH) and (4mL) of glacial CH₃COOH and cooling below 5°C) with continuous stirring in good ventilated hood. During addition, temperature was maintained at (15°C). By stirring the mixture for 3 hrs and kepping it at room temperature for one day. We get orange precipitate, which was washed with dilute HCl (0.20M) to take out any excess of KCN. The compound was recrystallized with 95% C₂H₅OH. The percentage yield of this procedure was (78.5%). The preparation way of the (L₂) ligand was illustrated in reaction below :



3. Preparation of [C₁-C₆] metal ion complexes⁹

A solution of (0.385gm, 1mmol) of the ligand (L₁) in (10mL) of ethanol (absolute) and solution of (0.343gm, 1mmol) of the ligand (L₂) in (15mL) of absolute C₂H₅OH was added by drop by drop to a solution of (0.267gm, 0.198gm, 0.270gm, 0.238gm, 0.237gm, 0.170gm) respectively, of the metal salts (0.001mol) of (CrCl₃.6H₂O, MnCl₂. 4H₂O, FeCl₃.6H₂O, CoCl₂.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O) respectively, in absolute C₂H₅OH with constant stirring. The resulting mixture was refluxed at (75 - 85)°C for four hrs and then the solution was left to be stirred 12 hrs at room temperature. A precipitate which was formed was filtered and then, the product was washed with methanol and ethanol and stored in desiccators.

4. The results and discussion

4.1. The physical properties of the prepared

ligand and complexes.

α -Aminonitrile ligand and its metal ion complexes were fully identified by elemental analysis (C.H.N.). The physical data were described in Table (1).

Table [1]: physical properties and elemental micro analysis of the prepared compounds

Cl % Calc . (Found)	M % Calc . (Found)	N % Calc . (Found)	H % Calc . (Found)	C % Calc . (Found)	m.p (°C)	coular	yield %	formula M.Wt g/mole	Comp
9.20 (8.97)	-----	10.89 (10.77)	5.44 (5.40)	52.88 (52.65)	255-257	Light White	-----	C ₁₇ H ₂₁ FCIN ₃ O ₄ 385.8)(	L ₁
10.36 (10.04)	-----	8.18 8.02)(	4.38 4.27)(	77.08 (76.91)	173-175	Orange	78.5	C ₂₂ H ₁₅ N ₂ Cl 342.5)(	L ₂
16.22 (15.97)	5.87 (6.04)	7.90 7.76)(	3.95 (3.29)	52.80 (52.65)	342 Dec.	Light green	76.7	[CrL ₁ L ₂ Cl(H ₂ O)] Cl.H ₂ O (886.3)	C ₁
11.78 11.56) (	6.08 5.94)(	7.75 (7.63)	4.95 (4.43)	51.78 (51.57)	334 Dec.	Yellow- green	77.6	[MnL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (903.74)	C ₂
15.10 (14.92)	5.94 (5.85)	7.45 (7.36)	4.89 4.48)(	49.78 (49.66)	349 Dec.	Yellow green	71.5	[FeL ₁ L ₂ Cl(H ₂ O)] Cl.2H ₂ O.CH ₃ OH (940.15)	C ₃
11.73 (11.43)	6.49 (6.39)	7.71 (7.53)	4.93 (4.67)	51.56 (51.44)	321-324	White red	78.8	[CoL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (907.73)	C ₄
11.74 (11.17)	6.47 (6.35)	7.71 (7.61)	4.81 (4.70)	51.57 (51.45)	316 Dec.	Gray	81.2	[NiL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (907.49)	C ₅
12.10 (12.22)	7.22 (7.13)	7.95 (7.82)	3.99 (4.02)	53.16 (52.97)	322 Dec.	Dark- green	75.6	[CuL ₁ L ₂ (H ₂ O) ₂] Cl.H ₂ O (880.35)	C ₆

Dec. = Decomposition

5. FT-IR spectra

5.1. FT-IR spectra of L₁ and L₂ ligands

The FT-IR data of the ciprofloxacin(L₁) and N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amine (L₂) were shown in Table (2) and Figures 1 and 2. The band at (1715) cm⁻¹ in the IR spectrum of the (L₁) ligand was recognized to the stretching vibration of the (C=O) group. The most significant stretching modes exhibited by (L₂) were correspond to by α-amino and nitrile groups. The band related to ν (C≡N) stretching vibration of the second ligand appeared at (2175) cm⁻¹.¹⁰ The band related to ν (N-H) stretching vibration appeared at (3388)cm⁻¹.¹¹ The band related to δ(N-H) bending vibration appear at (1578)cm⁻¹ of (L₁) and 1593 cm⁻¹ of (L₂).^{12,13} The bands assign to stretching vibrations of the ring and aliphatic (C-H) of the ligand appear at (3220) cm⁻¹ and (2948) cm⁻¹ respectively .

5.2. FTIR spectra of the (C₁-C₆) complexes

The band assigned to ν(C=O) group was observed at 1715 cm⁻¹ in the spectrum of (L₁) was observed either as a shoulder (C₂ and C₄) or as a weak peak (C₅).¹⁴ The absorption bands observed around (1488) cm⁻¹ equivalent to the stretching vibrations of (C=C) and (C=N) bonds appeared at a lower frequency in the spectra of complexes. The coordination by two oxygen atoms from ciprofloxacin molecule (one oxygen from pyridine and the other from the carboxylic group).¹⁵ The spectra of all [C₁ - C₆] complexes exhibit characteristic bands of either coordinated water appeared at (3430-3465)cm⁻¹ assigned to ν(OH) or lattice water appeared at (725-748) cm⁻¹ assigned to ρw (H₂O) in all complexes .¹⁶⁻¹⁸ New bands were observed in the region (422-471) cm⁻¹ and (510-565) cm⁻¹ assigned to ν (M - N) and ν (M-O) vibrations respectively.¹⁹ The band at (3388)cm⁻¹ which was assign to the ν(N - H) stretching vibration of the (N - H) group of (L₂) was shifted in the spectra of (C₁-C₆) complexes to (3335, 3360, 3357, 3337, 3348 and 3366) cm⁻¹ respectively, as shown in Figure 3 this gave an indication that the ligand was coordinated with the metal ions through the nitrogen atom of α-amino group. The band at (2175) cm⁻¹ which was assigned to the stretching vibration of ν (C≡N) group of (L₂) was shifted in the spectra of complexes (C₁ and C₃-C₆) to lower frequencies (2153, 2159, 2155, 2159 and 2161) cm⁻¹ respectively which refers to the linkage of (C≡N) group from nitrogen atom. The spectrum of the (C₂) complex was showed an increase shift in ν (C≡N) vibration towards to higher frequency as a result of coordination with metal ion through the lone pair electrons of nitrogen atom as shown in Figure 4, the decreases of ν (C≡N)

stretching vibration of complexes (C_1 and C_3 - C_6) were attributed to metal $d\pi$ to ligand $p\pi^*$ back-bonding but the increase of $\nu(C \equiv N)$ stretching vibration of (C_2) complex recognized to presence of π acceptor ligand.

Table[2]: TheCharacteristic infrared vibrations (cm^{-1}) of the ligands (L_1 and L_2) and their metal-ion complexes

Comp.	$\nu(N-H)$	$\nu(C \equiv N)$	$\nu(C=O)$	$\delta(N-H)$	$\nu(COO)$ (asy)	$\nu(COO)$ (sy)	$\nu(M-N)$	$\nu(M-O)$
L_1	3377 w.sh	-----	1715 v.sh	1578 s.sh	-----	-----	-----	-----
L_2	3388 m.sh	2175 m.sh	-----	1593 s.sh	-----	-----	-----	-----
C_1	3335 m.br	2153 m.sh	-----	1577 v.s.sh	1525 m.sh	1322 m.sh	528 w	471 w
C_2	3360 m.br	2205 m.sh	1685 sh	1591 s.sh	1544 m.sh	1294 s.sh	537 w	427 w
C_3	3357 w.br	2159 m.sh	-----	1589 v.sh	1549 s.sh	1371 s.sh	510 w	422 w
C_4	3337 w.br	2155 v.s.sh	1681 sh	1581 m.sh	1566 s.sh	1287 m.sh	549 w	445 w
C_5	3348 s.br	2159 m.sh	1679 s	1575 sh	1538 m.sh	1313 m.sh	565 w	425 w
C_6	3366 m.br	2161 w.sh	1682 sh	1602 v.s.sh	1529 w.sh	1289 m.sh	547 w	435 w

Where: s = strong, m = medium, w = weak, v = very, br = broad, sh = sharp

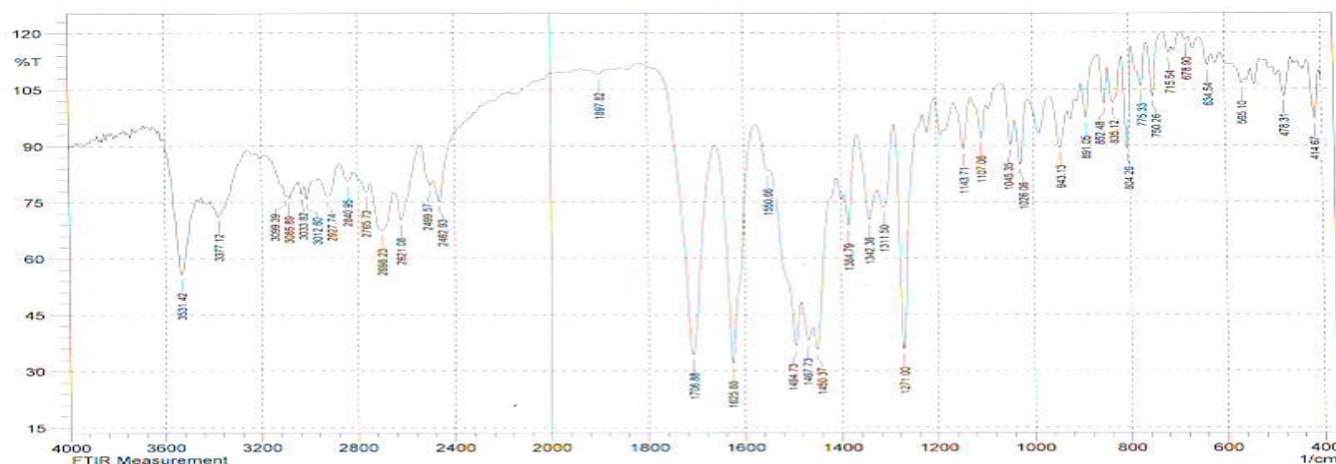


Fig. (1): FT - IR spectrum of [L_1]

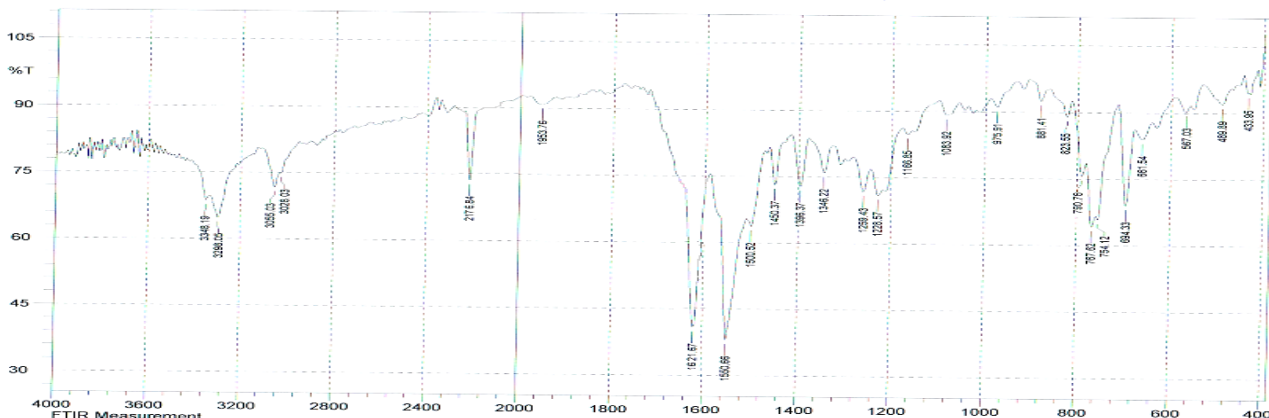
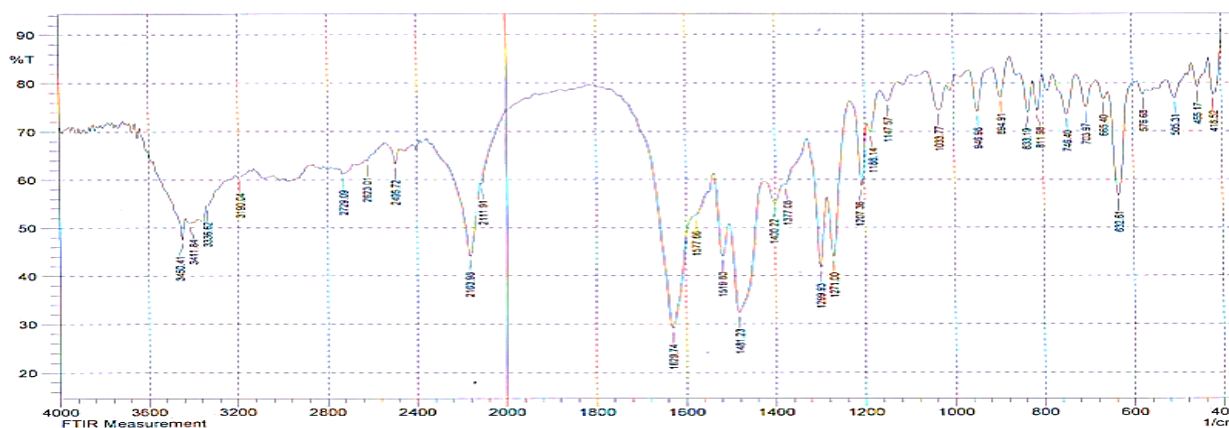
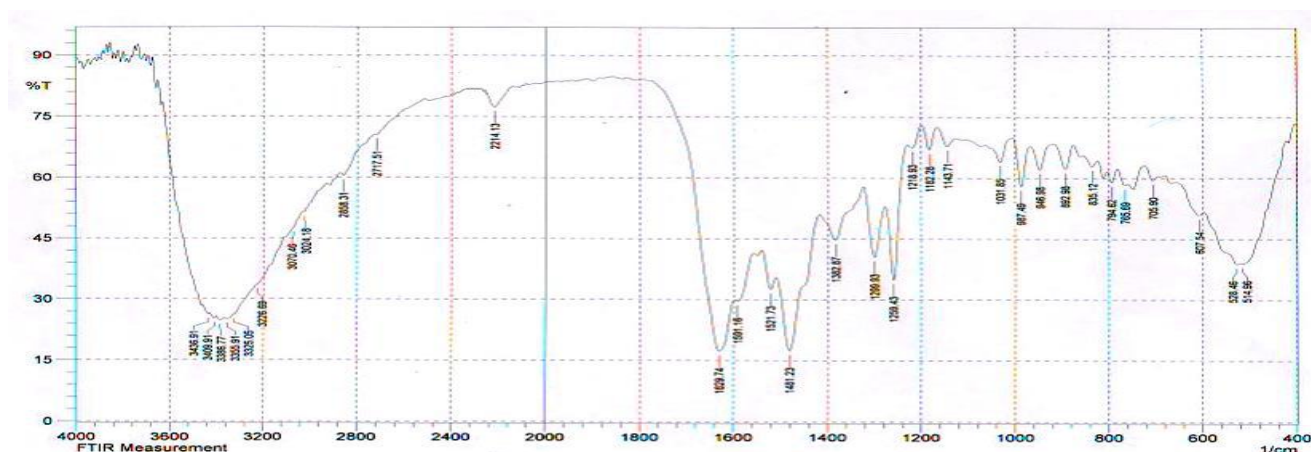


Fig. (2): FT - IR spectrum of [L₂]

 Fig. (3): FT - IR spectrum of [C₁]

 Fig. (4): FT - IR spectrum of [C₂]

6. ¹H-NMR and ¹³C-NMR spectra

6.1. ¹H-NMR

The ligand (L₂) was characterized by ¹H-NMR and ¹³C-NMR spectroscopic methods as shown in Figure 5 and 6 in addition to all the six metal-ion complexes (C₁-C₆) using DMSO (d₆) as shown in Table (3). The ¹H-NMR spectrum of the ciprofloxacin was showed five peaks; the first peak was appeared at δ(1.51) ppm which assigned to the (-CH₂-), the second one was appeared at δ(3.13) ppm was assigned to the (-NH) proton whereas the third one was appeared at δ(3.31) ppm which assigned to (-CH₂-N-).²¹ The forth one was appeared at δ(7.66-7.78)ppm was attributed to the ring protons and the last peak was appeared at δ(8.99)ppm was attributed to the (-COOH).²² The ¹H - NMR spectrum of the (L₂) ligand was showed four peaks, the first peak was appeared at δ(2.78) ppm which was attributed to the peak of the solvent (dimethyl sulfoxide) the second one which was appeared at δ(3.05) ppm was attributed to the (-NH) proton whereas the third one was appeared at δ(5.50) ppm which corresponded to (-CHC≡N) proton. The final one which was appeared at δ(6.49 - 7.98) ppm was assigned to the ring protons.^{18,20} The ¹H-NMR spectra of the complexes (C₁ - C₆) were alike to that of the ligands. The only three difference were that the signal of (-NH) of the ligand was shifted in these compounds by (0.36, 0.28, 0.67, 0.55, 0.48 and 0.41) ppm respectively and the indication of (-CHC≡N) was shifted in these compounds by (0.19, 0.18, 0.31, 0.25, 0.46 and 0.17) ppm respectively. This gave a suggestion for complex structure.

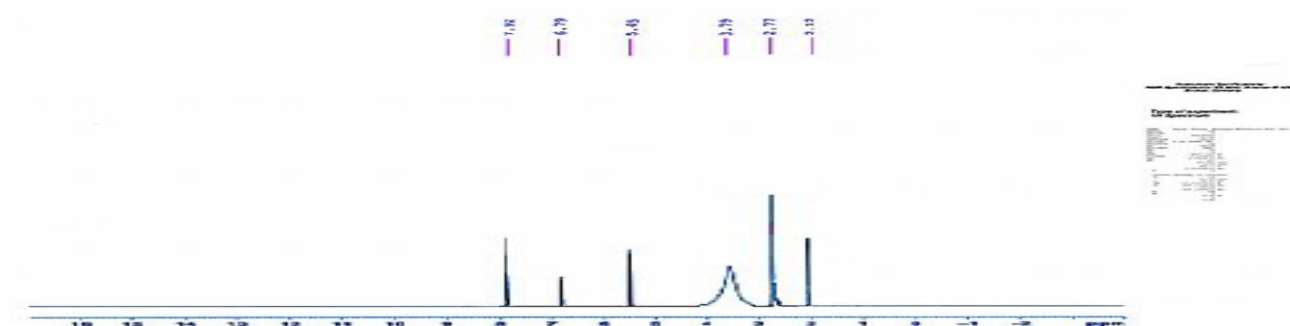


Fig. (5): ¹H - NMR spectrum of [L₂]

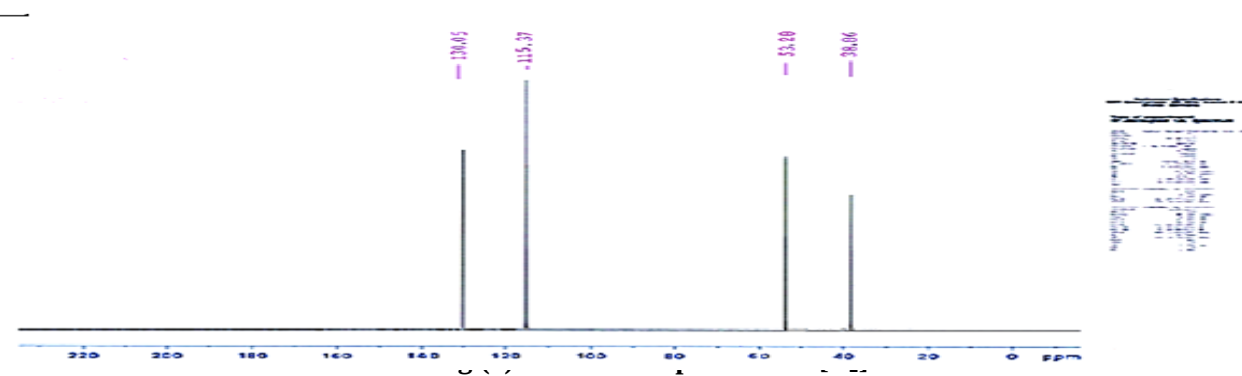


Fig. (6): ¹³C- NMR spectrum of [L₂]

6.2. ¹³C-NMR spectra

L₁ and L₂ ligands were characterized by ¹³C-NMR spectroscopic methods, as well as all the complexes (C₁-C₆) using DMSO (d₆) as shown in Table (3). The ¹³C-NMR band of the ciprofloxacin ligand (L₁) showed seven peaks; the first one was appeared at (7.8) ppm which was corresponded to the (-CH₂-CH₂-). The second one was appeared at δ(35.08) ppm was corresponding to the (-CHN=) carbon, the third band which was appeared at (45.08) ppm was assigned to the (-CH₂-NH-) carbon the forth band which was appeared at δ(52.1) ppm was assigned to the (-CH₂-N-) carbon, the fifth one which was appeared at δ(166.02) ppm was assigned to the (-COOH) carbon, the sixth one which was appeared at δ(176.04) ppm was assigned to the (>C=O) carbon and the last one appeared at δ(103-116) ppm was assigned to the aromatic carbon atoms.^{20,21} The ¹³C-NMR spectrum of (L₂) was showed four characteristic peaks; the first one was shown at δ(38.86) ppm was corresponded to the solvent peak (DMSO), the second peak appeared at (54.42) ppm was attributed to the (-CH-C≡N) carbon and the last peak appeared at δ(116.17) ppm was assigned to the (-CH-C≡N) carbon atom.²¹ The ¹³C-NMR spectrum of the complexes (C₁-C₆) was like to that of the ligand. The only differentiation was that the sign of (-NH-CH-C≡N) carbon of the ligand was shifted in these complexes by (0.07, 1.81, 5.00 and 4.48) ppm respectively, the signal of (-CH-C≡N) carbon was shifted in these complexes by (1.83, 2.11, 5.71 and 4.58) ppm and the sign of (>C=O) carbon was shifted in these complexes by (1.29, 0.86, 3.03, 2.24, 2.74 and 2.04) ppm and the signal of (-COOH) carbon was shifted in these compounds by (0.55, 0.89, 1.73, 1.81, 0.94 and 0.91) ppm respectively, this gave another indication for complexes formation.

Table (3): ^1H -NMR and ^{13}C -NMR of the ligands(L_1 and L_2) and some of their metal ion complexes

Compound	Formula	Group	Chemical Shifts $\delta(\text{ppm})$	Group	Chemical Shifts $\delta(\text{ppm})$
L_1	$\text{C}_{17}\text{H}_{21}\text{FClN}_3\text{O}_4$	($-\text{CH}_2-\text{CH}_2-$) ($=\text{CH}-\text{N}=\text{N}$) ($-\text{CH}_2-\text{NH}-$) ($-\text{CH}_2-\text{N}=\text{N}$) Ar-H ($-\text{COOH}$) ($>\text{C}=\text{O}$)	7.80 35.08 45.08 52.01 103-116 166.02 176.04	($-\text{CH}_2-$) ($=\text{NH}$) ($-\text{CH}_2-\text{N}=\text{N}$) (Ar-H) ($-\text{COOH}$)	1.51 3.13 3.31 7.66-8.68 8.99
L_2	$\text{C}_{22}\text{H}_{15}\text{N}_2\text{Cl}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$)	54.42 116.17	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H)	3.05 5.36 6.49-7.98
C_1	$[\text{CrL}_1\text{L}_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}\cdot\text{H}_2\text{O}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	53.13 117.03 165.47 177.26	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.41 5.55 6.31-7.56 8.98
C_2	$[\text{MnL}_1\text{L}_2\text{Cl}(\text{H}_2\text{O})]2\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	53.27 117.03 165.13 177.26	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.33 5.54 6.31-7.56 8.97
C_3	$[\text{FeL}_1\text{L}_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}\cdot 2\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	51.39 113.26 164.29 176.26	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.72 5.67 6.12-7.56 8.99
C_4	$[\text{CoL}_1\text{L}_2\text{Cl}(\text{H}_2\text{O})]2\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	52.18 113.26 164.21 176.26	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.66 5.61 6.33-7.69 8.98
C_5	$[\text{NiL}_1\text{L}_2\text{Cl}(\text{H}_2\text{O})]2\text{H}_2\text{O}\cdot\text{CH}_3\text{OH}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	51.68 119.95 165.08 175.91	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.53 5.82 6.82-7.97 8.84
C_6	$[\text{CuL}_1\text{L}_2(\text{H}_2\text{O})_2]\text{Cl}\cdot\text{H}_2\text{O}$	($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{CH}-\text{C}\equiv\text{N}$) ($-\text{COOH}$) ($>\text{C}=\text{O}$)	52.35 120.91 165.11 175.26	($=\text{NH}$) ($=\text{CH}-\text{C}\equiv\text{N}$) (Ar-H) ($-\text{COOH}$)	3.46 5.53 6.21-7.98 8.96

7. Electronic spectra (UV-Vis.)

7.1. Electronic spectra of the ligands

The electronic spectra of the ligands (L_1 , L_2 and L_1L_2) and their metal-ion complexes were recorded in $\text{C}_2\text{H}_5\text{OH}$ at room temperature and their assignments given in Table (4), while their spectra were shown in Figures (7 and 8). The spectra of two ligands exhibited high intensity bands appeared in the region (35587 and 33898) cm^{-1} respectively, assign to $\pi \rightarrow \pi^*$ of conjugated system.²⁴ Low intensity bands appeared at lower energy (31546 and 27701) cm^{-1} respectively, were assign to $n \rightarrow \pi^*$ transition. The assignments of (L_1L_2) ligands exhibited high intensity bands appeared in the region (46512) cm^{-1} was assigned to $\pi \rightarrow \pi^*$ of conjugated system.¹⁹ Low intensity band appeared at lower energy (29851) cm^{-1} was assign to $n \rightarrow \pi^*$ transition. The intensity and position of this band was depending on the structure of molecules and the nature of the solvent used.²⁵ The electronic spectra of some complexes exhibited new bands, with intensities and positions of these bands are generally dependent on ligand field effects, stereochemistry of complexes and electron configuration of metal-ions.²⁵

7.2. Electronic spectra of (C_1 - C_6) complexes

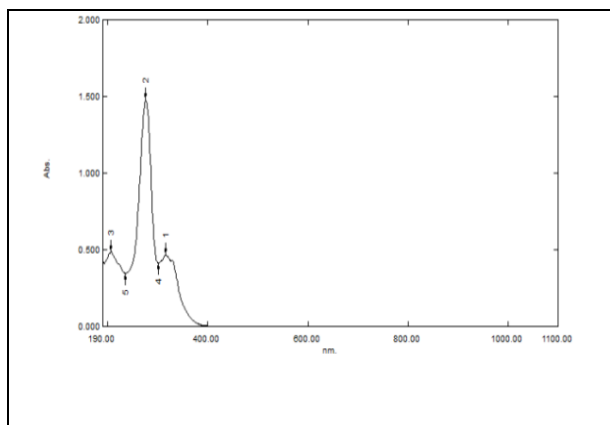
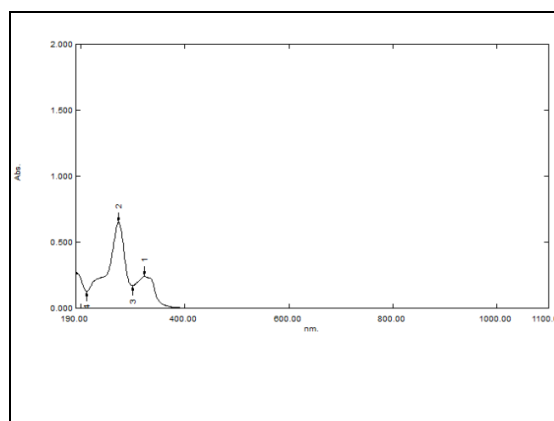
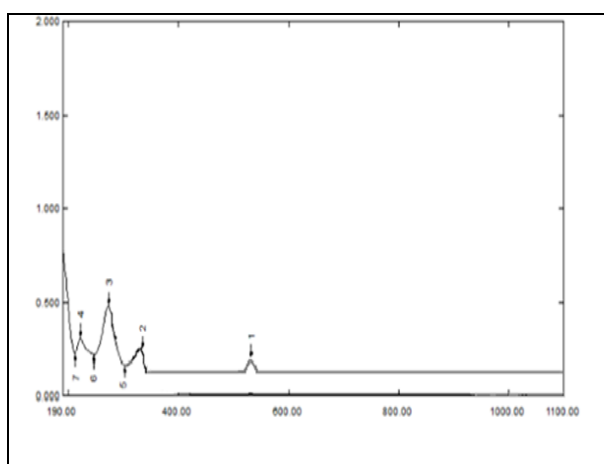
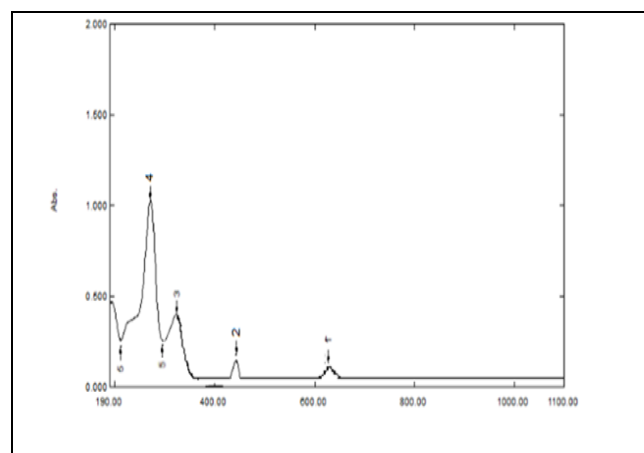
The spectrum of the Cr^{III} complex (C_1) was showed two (d - d) bands of transition which are observed at (16026 and 21930) cm^{-1} , these two bands possibly assign to the transitions $\nu_2(^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g}(\text{F}))$ and $\nu_3(^4\text{A}_{2g} \rightarrow ^4\text{T}_{1g}(\text{p}))$ respectively, in an octahedral geometry around the Cr^{III} ion. The $\nu_1(^4\text{A}_{2g} \rightarrow ^4\text{T}_{2g})$, transition is probable to appear at longer wavelength, it was calculated in theory through the Tanabe - Sugano diagram. The magnetic moment value (4.77) B.M was in accordance with those having octahedral structure²⁶ as shown in

Figure 9. The spectrum of the complex (C₂) was showed one band of (d-d) transition observed at (18484) cm⁻¹ as shown in Figure 10, this band may be assigned to the transition $\nu(^6A_{1g} \rightarrow ^4T_{1g}(G))$. The (5.59) B.M magnetic moment value was in agreement with those having octahedral complexes.²⁶ The spectrum of the complex (C₃) was showed 2 bands of (d-d) transition wrer observed at (13605 and 20284) cm⁻¹, these bands may be assigned to the transitions $\nu_1(^6A_{1g} \rightarrow ^4T_{2g}(G))$ and $\nu_2(^6A_{1g} \rightarrow ^4A_{1g} + ^4E_g)$. The (5.44) B.M magnetic moment value was in agreement with those having high spin Fe (III) octahedral complexes.²⁷ The spectrum of the Co(II) complex (C₄) was showed three bands of (d-d) transition observd at (10989, 16921 and 19841) cm⁻¹ respectively, these bands may be assigned to the transitions $\nu_1(^4T_{1g}(F) \rightarrow ^4T_{1g}(P))$, $\nu_2(^4T_{1g}(F) \rightarrow ^4A_{2g})$ and $\nu_3(^4T_{1g}(F) \rightarrow ^4T_{2g}(F))$. The (4.16) B.M magnetic moment value was in agreement with those having octahedral structure.²⁷ The spectrum of the complex (C₅) was showed two bands of (d-d) shift observed at (16313 and 21413) cm⁻¹ these bands possibly assigned to the transitions $\nu_1(^3A_{2g} \rightarrow ^3T_{2g})$ and $\nu_2(^3A_{2g} \rightarrow ^3T_{1g}(p))$. The value of the magnetic moment (2.75) B.M was in agreement with those having octahedral structure.²⁹ The spectrum of the complex (C₆) was showed one (d-d) band transition observed at (20202) cm⁻¹ this band may be assign to the transition $\nu(^2E_g \rightarrow ^2T_{2g})$. The (1.87) B.M magnetic moment value was in agreement with those having distorted octahedral structure.³⁰

Table(4):Electronic spectral data, magnetic moment, of the studied complexes and two ligands

Geometry Suggested	B.M()	¹ cm ⁻¹ 15B ⁻¹	Dq/B -	β	B ⁻ cm ⁻¹	Molar conductance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$	Assignment	ν -cm ⁻¹	nm) λ	Compound
-----	-----	-----		-----	-----	-----	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	31546 35587	317 281	L ₁
-----	-----	-----		-----	-----	-----	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	28169 33898	355 295	L ₂
-----	-----	-----		-----	-----	-----	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	29851 46512	335 215	L ₁ L ₂
Octahedra l	4.77	10531	2.32	0.773	710	43.9	$^4A_{2g} \rightarrow ^4T_{2g}$ $^4A_{2g} \rightarrow ^4T_{1g}(F)$ $^4A_{2g} \rightarrow ^4T_{1g}(P)$	16026 21930 31640*	624 456 -----	C ₁
Octahedra l	5.59	-----	-----	-----	-----	20.9	$^6A_{1g} \rightarrow ^4T_{1g}(G)$	18484	541	C ₂
Octahedra l	5.44	-----	-----	-----	-----	27.5	$^6A_{1g} \rightarrow ^6T_{1g}(G)$ $^6A_{1g} \rightarrow ^4A_{1g} + ^4E_g$	13605 20284	735 493	C ₃
Octahedra l	4.16	-----	-----	-----	-----	18.7	$^4T_{1g}(F) \rightarrow ^4T_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ $^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$	10989 16921 19157	910 591 504	C ₄
Octahedra l	2.75	-----	-----	-----	-----	22.8	$^3A_{2g} \rightarrow ^3T_{2g}$ $^3A_{2g} \rightarrow ^3T_{1g}(p)$	16313 21929	613 467	C ₅
Distorted Octahedra l	1.87	-----	-----	-----	-----	33.3	$^2E_g \rightarrow ^2T_{2g}$	19607	495	C ₆

Calc. = Calculated value *


Fig.(7): UV-Vis. spectrum of [L₁]

Fig.(8): UV-Vis. spectrum of [L₂]

Fig.(9): UV-Vis. spectrum of [C₁]

Fig.(10): UV-Vis. spectrum of [C₂]

8. Thermal analysis of (C₁-C₆) metal-ion complexes

Thermal decomposition of complexes (C₁-C₆) were obtained following TG techniques at heating range (30-450) °C and heating rate (10 °C /min) used gas nitrogen. The thermal decomposition information for the (C₁-C₆) complexes (3 steps) were given in Table (5).The following results was obtained:

1. The first stage which took place at temperature range of (70-150) °C. includes departure of the methanol and Lattice water molecules.^{31,32}
2. The following stage at temperature range of (140-215) °C includes departure of the coordinated water molecules and chloride ions at temperatures were depending on the bond energies resulted from coordination of ligand atoms .^{33,34}
3. The third stage (215-380) involved the departure of some other fragments of the ligands. However because of the limited heating range, the decomposition was incomplete for all complexes leaving the metal ion still coordinated to the remaining parts of the ligands.^{35,36}

Table (5): Thermal decomposition data for some complexes

Comp.	Molecular formula	Step	Temp. rang of the Decomposition°C	Suggested Formula of loss	Mass loss% Cal. found	
C ₁	[CrL ₁ L ₂ Cl(H ₂ O)] Cl.H ₂ O (886.3)	1	70-140	Cl, H ₂ O.	6.04	5.87
		2	140-215	Cl, H ₂ O	6.04	5.63
		3	215-380	C ₂₆ H ₂₄ FClN ₅ O ₃ Residue	57.37 30.63	56.45 29.56
C ₂	[MnL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (903.74)	1	60-135	2H ₂ O.CH ₃ OH	7.52	6.97
		2	135-205	Cl, H ₂ O	5.92	5.33
		3	205-370	C ₂₉ H ₂₅ FClN ₅ O ₃ Residue	59.70 26.86	59.45 26.56
C ₃	[FeL ₁ L ₂ Cl(H ₂ O)] Cl.2H ₂ O.CH ₃ OH (940.15)	1	85-155	2H ₂ O.CH ₃ OH	7.23	7.01
		2	155-185	Cl, H ₂ O	5.69	5.22
		3	185-375	C ₂₈ H ₂₈ FCl ₂ N ₅ O ₃ Residue	60.31 26.77	58.90 26.14
C ₄	[CoL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (907.73)	1	121-197	2H ₂ O.CH ₃ OH	7.49	7.19
		2	197-305	Cl, H ₂ O	5.89	5.75
		3	305-355	C ₂₇ H ₂₈ FCl ₂ N ₅ O ₃ Residue	61.03 25.59	60.45 24.88
C ₅	[NiL ₁ L ₂ Cl (H ₂ O)] 2H ₂ O.CH ₃ OH (907.49)	1	75-145	2H ₂ O.CH ₃ OH	7.49	7.32
		2	145-180	Cl, H ₂ O	5.90	5.45
		3	180-385	C ₂₆ H ₂₇ FClN ₅ O ₃ Residue	55.70 30.91	54.24 29.34
C ₆	[CuL ₁ L ₂ (H ₂ O) ₂] Cl.H ₂ O (880.35)	1	75-145	Cl, H ₂ O	6.08	5.69
		2	145-180	Cl, 2H ₂ O	8.12	7.77
		3	180-385	C ₂₈ H ₂₈ FClN ₅ O ₃ Residue	55.60 30.20	54.24 29.45

9. In vitro antibacterial activity

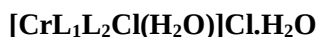
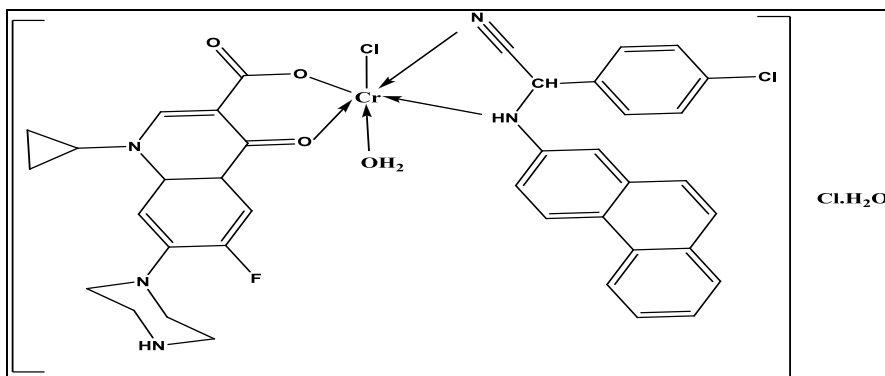
The antibacterial activities of all the metal ion complexes were screen against test bacteria namely; *Staphylococcus aureus*, *Bacillus subtilis* (Gram+), *Escherichia* and *Pseudomonas aerugin* (Gram-). Agar,(well-diffusion method) used to find out the activity.³⁶ Borer of (0.6 mm) diameter was used. The concentration of all the metal ion complexes was (0.001M) using (DMSO) which was used as a control Gram- while ciprofloxacin was used as a control Gram+. The solvent was showed inactivity against the tested bacteria, but some of the prepared metal ion complexes were showed very good results.³⁸ The inhibition zones of the solvent and the prepared complexes were shown in Table (6).The inhibition zones were calculated in (mm) and compare to the inhibition zone of the broad spectrum antibiotic. All the metal ion complexes show activity against the (Gram-) bacterium (*Escherichia coli*), which can cause disease, for example, enter toxigenic strain produce a poison in the gut, resulting normally in diarrhea.³⁹ The complexes (C₁ and C₃) show highest activity against *Pseudomonas*. This bacterium was known for its resistance to most of the developed antibiotics and was recognized to be the major case of many health issues and infections.⁴⁰ All of those experiments relative to parent antibiotic ciprofloxacin derivatives, and then we observed that the complexes (C₁ and C₄) was showed better activities than ciprofloxacin adjacent to (Gram+) organisms such as *Staphylococcus aureus* and *Streptococci*. Whereas the complexes (C₂ and C₄) exhibited similar activity against *Staphylococcus* and the meta ion complexes (C₁, C₃ and C₅) also showed similar activities against *Streptococci*. The metal ion complexes (C₁, C₃, C₄ and C₅) showed highest activity against *Pseudomonas*, with highest activity by (C₄) exhibited better activity the others. The Cr^{III} complex was showed higher activity against the gram negative bacterium (*Escherichia coli*), compound with the other complexes. Many factors were used to control the biological activities of the metal-ion complexes.⁴¹ Type of ligand, kind of the metal, charge of complex, the transition metal series, and electronic structure of the metal-ion and shape of the metal-ion complexes are affected on biological activity.⁴²

Table (6): Inhibition zones calculated in (mm) of DMSO , ciprofloxacin and the complexes

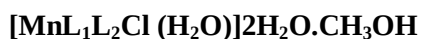
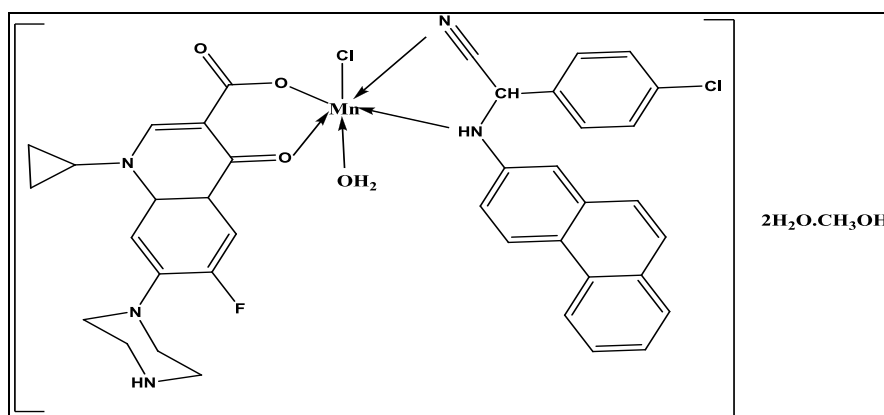
Comp.	Inhibition zone (mm) <i>Escherichia coli</i>	Inhibition zone (mm) <i>Pseudomonas aeruginosa</i>	Inhibition zone (mm) <i>Staphylococcus aureus</i>	Inhibition zone (mm) <i>Streptococci</i>
DMSO	///	///	///	///
(ciprofloxacin)	19.50	24.86	18.15	14.12
C ₁	20.00	45.25	25.12	19.23
C ₂	9.00	17.76	7.50	14.22
C ₃	12.00	35.00	7.22	14.13
C ₄	9.00	46.33	24.87	18.80
C ₅	12.00	25.25	6.00	14.21
C ₆	10.04	18.08	7.52	12.65

10. The Proposed molecular structure

The proposed molecular structure of the prepared compounds were established by their elemental analysis (CHN), TGA, FTIR, ¹H-NMR and ¹³C-NMR spectra, electronic spectra' as well as by molar conductance data. According to the study obtained the structures of the metal-ion complexes were recommended as shown in Figures (11-16) below:

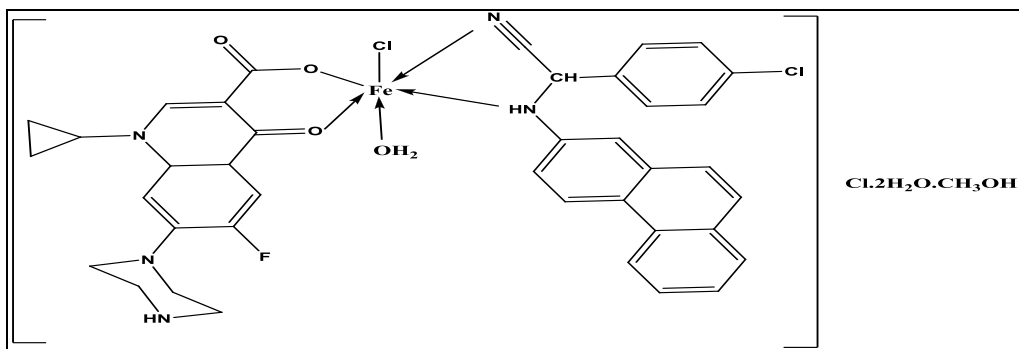


[Chloro aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} chrome (III)] chloride hydrate

Fig.(11): Suggested structure of [C₁]


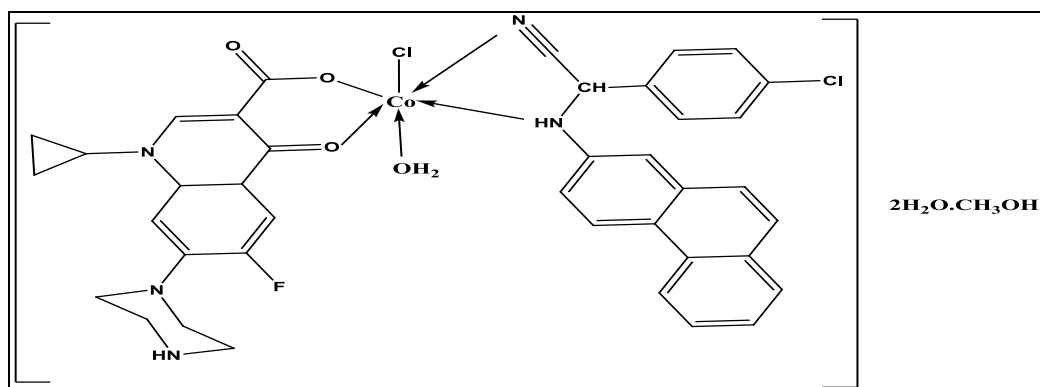
[Chloro aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} manganese (II)] chloride (2) hydrate methanol

Fig. (12): Suggested structure of [C₂]



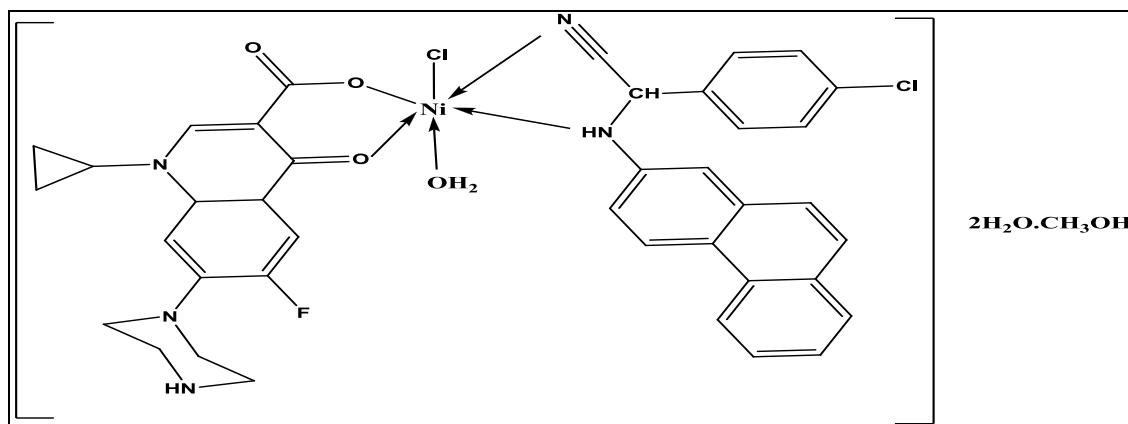
[Chloro mono aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} iron (III)] chloride (2) hydrate methanol

Fig.(13): Suggested structure of [C₃]



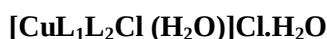
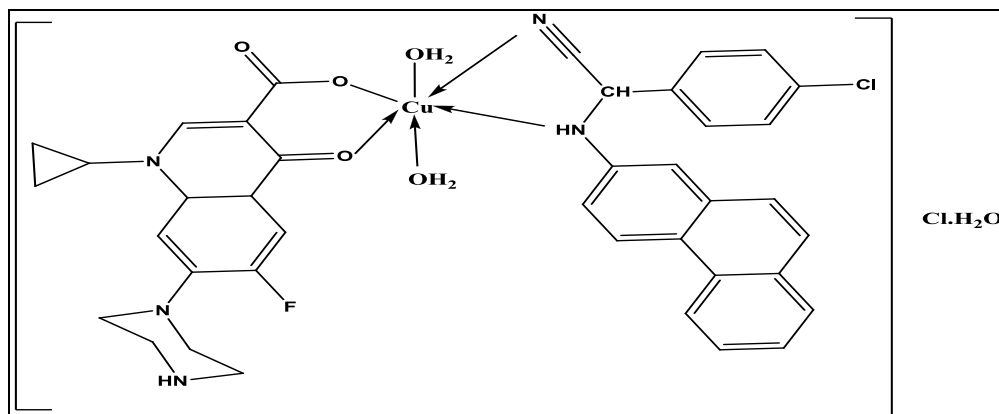
[Chloro mono aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} cobalt (II)] chloride (2) hydrate methanol

Fig.(14): Suggested structure of [C₄]



[Chloro mono aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} nickel (II)] chloride (2) hydrate methanol

Fig.(15): Suggested structure of C₅



[Chloro aqua ciprofloxacin {N-(1-(4-chlorophenyl)prop-2-ynl)phenanthren-2-amino} copper (II)] chloride hydrate

Fig.(16): Suggested structure of [C₆]

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