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Metal complexes of mixed ligands (quinolone antibiotics and α-aminonitrile derivatives) their applications: an update with Mn(II), Cu(II) and Cr(III) ions and study the biological activity

Saad Khudhur Mohammed*, Mohammed H.A.Al-Amery
Baghdad University, College of Science, Department of Chemistry, Baghdad, (IRAQ)
E-mail: musabali33@yahoo.com

ABSTRACT

Quinolones (ciprofloxacin) are synthetic broad-spectrum antibiotics with good oral absorption and excellent bioavailability. Due to the chemical functions found on their nucleus (a carboxylic acid function at the 3-position) and in most cases a basic piperazinyl ring (or another N-heterocycle) at the 7-position and a carbonyl oxygen atom at the 4-position) quinolones bind metal ions forming complexes which they can act as bidentate. Bidentate ligands L_2=2-phenyl-2-(1-Naphthylamine) acetonitrile was prepared by the reaction of Primiry amine with benzaldehyde, in presence of potassium cyanide and acidic media. The metal complexes were characterized by the micro element analysis (C.H.N.), chloride content, ^{1}H-NMR, ^{13}C-NMR, FTIR and UV-Vis spectra, molar conductivity as well as magnetic susceptibility measurement. The coordination chemistry and bonding behaviors of the metal ions and ligands has been studied according to the spectra of the complexes on UV-vis and IR regions. According to the obtained data the probable coordination geometries of these complexes were suggested as octahedral. Some complexes were found to be non-electrolyte others were found to be weak electrolyte. The following metal ion complexes were prepared along with their suggested formulae base on the following: The metal ion complexes of the ligands (L_1 and L_2) by condensation a solution mixture of [Mn(II), Cu(II) and Cr(III)] ions respectively, in absolute ethanol with stirring gave the formulae: $[ML_1L_2\ Cl(H_2O)_x].2H_2O$ Where M:{Mn^{2+} or Cu^{2+}}, x=1 or 2 and $[CrL_1L_2Cl(H_2O)]Cl.3H_2O$.

KEYWORDS

Quinolones (ciprofloxacin) 2-phenyl-2- (1-Naphthylamine) acetonitrile transition metal ions.

INTRODUCTION

The utility of quinolone derivatives in areas of medicine, food, catalyst, dye, materials, refineries and electronics is well established. 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[1]. In their metal complexes, the quinolones can act as bidentate ligand, as unidentate ligand and as bridging ligand. Frequently, the quinolones are coordinated in a bidentate manner, through one of the oxygen atoms of deprotonated carboxylic group and the ring car-

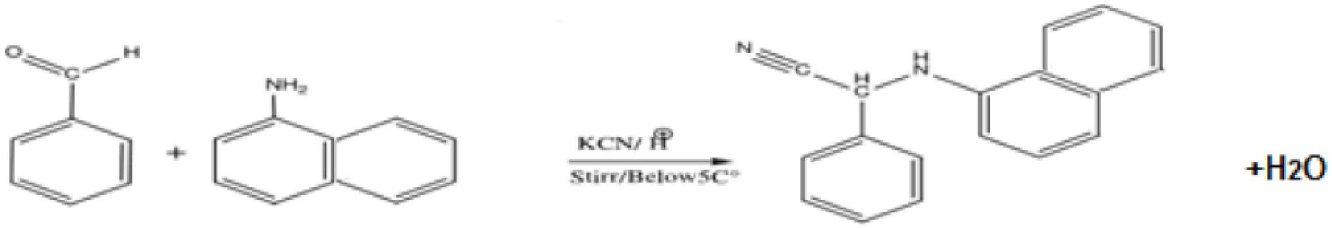
bonyl oxygen atom. The generic term "quinolone antibiotics" refers to a group of synthetic antibiotics with bactericidal effects, the first compound of the series, was introduced in therapy in the 1960s[2]. The clinical use of nalidixic acid was limited by its narrow spectrum of activity. Several modifications 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 position 7 and introduction of a fluoride atom at the position 6[3]. the new 4-quinolones, fluoroquinolones, have been discovered starting in the 1980s[4].

Preparation of the Ligand

The ligand (L_2) was prepared by following a previously reported except changing of primary aromatic amine (1-Naphthylamine). Potassium cyanide (0.13g,0.002mol) was dissolved in (4mL) of distilled water and cooled below 5°C. To this solution, Benzaldehyde (0.212g, 0.002mol) in (25mL of 95% ethanol) was added. The mixture was stirred maintaining temperature below 5°C. Glacial acetic acid (0.12g, 0.002mol) was added with constant stirring keeping temperature below 5°C, this was followed by the addition of 1-Naphthylamine (0.286g, 0.002mol) in (10mL of 95% ethanol) and (5mL) of Glacial acetic acid (cooled below 5°C) with continuous stirring in well ventilated hood. During addition, temperature was maintained at (15°C). The mixture was stirred for 2 hrs and was kept at room temperature for 24 hrs[5]. The obtained long (Purple) needles, were washed with diluted hydrochloric acid (0.2M) to remove any excess of cyanide[5]. The compound was re-crystallized with 95% ethanol. The yield percentage of this procedure was (70.9%). The synthesis route of the ligand is illustrated in reaction below:-

Preparation of complexes(C_1-C_3)

Preparation of (C_1) complex: a solution of (0.385g, 1mmol) of ciprofloxacin ligand (L_1) in (10mL) of absolute ethanol and (0.258g, 1mmol) of ligand (L_2) in (10mL) of absolute ethanol was added drop wise to a solution of 1mmol of metal chloride(0.170g 0.197g and 0.266g,) for ($CuCl_2.2H_2O$, $MnCl_2.4H_2O$ and $CrCl_3.6H_2O$ respectively) dissolved in (20mL) of absolute ethanol and refluxed with stirring under anhydrous conditions



Benzaldehyde **1-Naphthylamine** **2-phenyl-2-(1-Naphthylamine)acetonitrile (L_2)**

TABLE 1 : Elemental micro analysis and some physical properties of the ligands (L_1 and L_2) and their prepared complexes

Comp.	Formula M.W.T	Yield %	Color	M.P (°C)	C % CAL (Found)	H % CAL (Found)	N % CAL (Found)	M % CAL (Found)	Chlorine %
L_1	$C_{17}H_{21}FClN_3O_4$ (385.8)	-----	Light White	255-257	52.87 (52.20)	5.44 (5.13)	10.88 (10.07)	------	9.18 (8.65)
L_2	$C_{18}H_{14}N_2$ (258)	70.9	Purple	152-155	83.72 (82.33)	5.42 (5.17)	10.85 (10.00)	------	------
C_1	$[MnL_1L_2Cl(H_2O)].2H_2O$ (733.7)	86.9	Yellow-green	318 Dec.	57.24 (55.73)	3.95 (3.29)	9.54 (7.63)	7.48 (6.04)	4.83 (3.86)
C_2	$[CuL_1L_2(H_2O)_2].Cl.2H_2O$ (751.3)	67.8	Dark green	298 Dec.	55.90 (54.38)	3.99 (3.02)	9.58 (8.06)	8.45 (7.03)	4.71 (3.56)
C_3	$[CrL_1L_2Cl(H_2O)]Cl.3H_2O$ (783.3)	60.5	Light Green	362 Dec.	53.61 (51.95)	3.95 (2.99)	8.93 (7.83)	6.62 (5.48)	9.05 (8.81)

Dec. Decomposition

TABLE 2 : Characteristic infrared absorption bands of ligands ($L_1$and L_2) and their metal ions complexes

Comp.	υ(N- H) cm^{-1}	υ(C=N) cm^{-1}	υ(c=o) cm^{-1}	δN- H cm^{-1}	υ(c-o-c) (asy) cm^{-1}	υ(c-o-c) (sy) cm^{-1}	υ(M-N) cm^{-1}	υ(M-O) cm^{-1}
L_1	3377 w.sh	------	1706 v.sh	1625 s.sh	------	------	-----	-----
L_2	3363 m.sh	2189 m.sh	------	1605 s.sh	------	------	-----	-----
C_4	3315 m.br	2157 m.sh	------	1627 s.sh	1571 s.sh	1267 m.sh	545 w	428 w
C_5	3351 m.br	2177 w.sh	------	1629 v.s.sh	1518 m.sh	1303 m.sh	557 w	430 w
C_6	3385 m.br	2214 m.sh	------	1629 v.s.sh	1521 w.sh	1299 m.sh	514 w	480 w

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

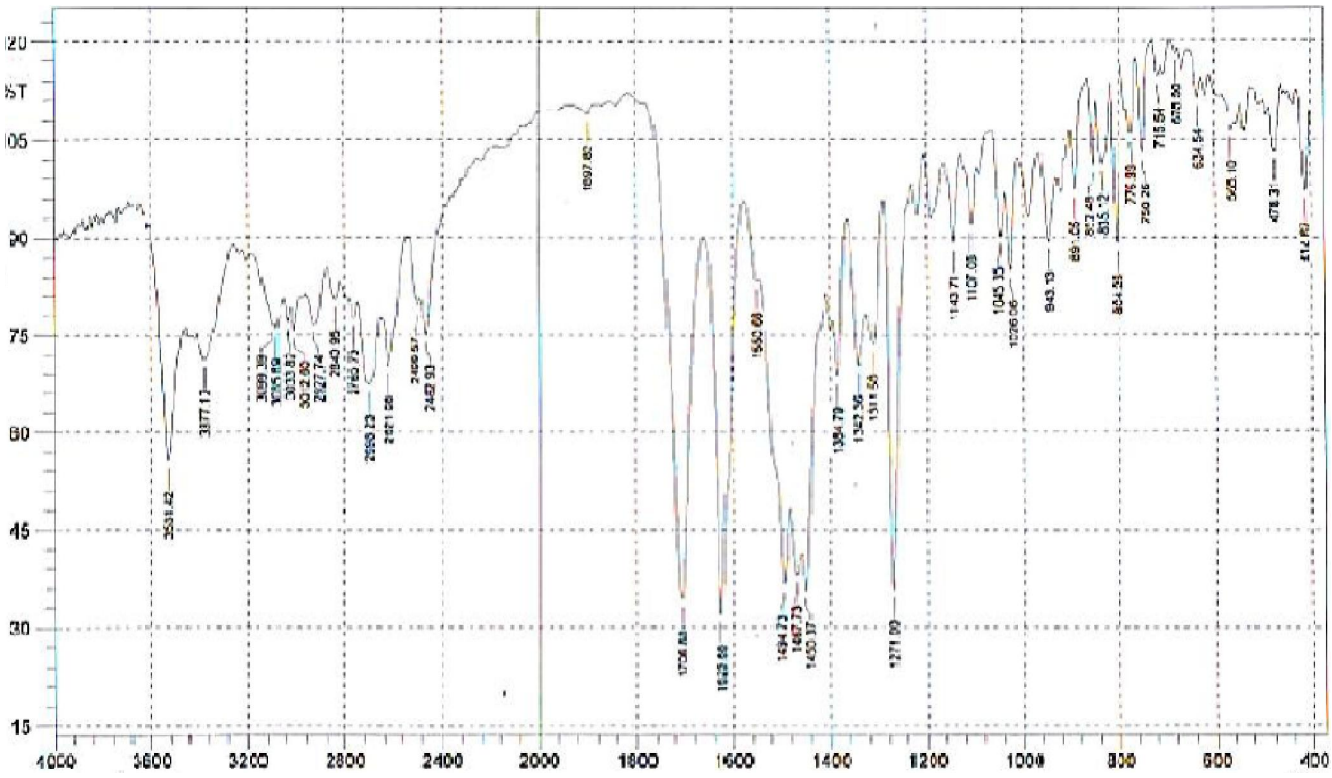


Figure 1 : FTIR spectrum of L_1

using Na_2SO_4 (anhydrous) for 24 hrs. The obtained complexes were collected after evaporation and the products were left in the desiccator to be dried under P_2O_5.

RESULTS AND DISCUSSION

The importance of preparing α-aminonitrile compounds arises from their versatility as starting materials for the synthesis of many compounds[8]. The structures of prepared α-aminonitriles were identified by C.H.N. (TABLE 1), FTIR((TABLE 2), ^{1}H-NMR and ^{13}C-NMR Spectra(TABLE 3) UV-visible (TABLE 4) techniques.

FTIR SPECTRA

Ciprofloxacin and α-Aminonitrile ligands

The FTIR spectral data of ciprofloxacin (L_1) and α-aminonitrile ligand (L_2) were shown in TABLE (2) and their spectra were shown in Figures (1 and 2). Both ligands showed the features: The band at (1706 cm^{-1}) which was assigned to the υ(C=O) stretching vibration of the carboxylic group (L_1) and

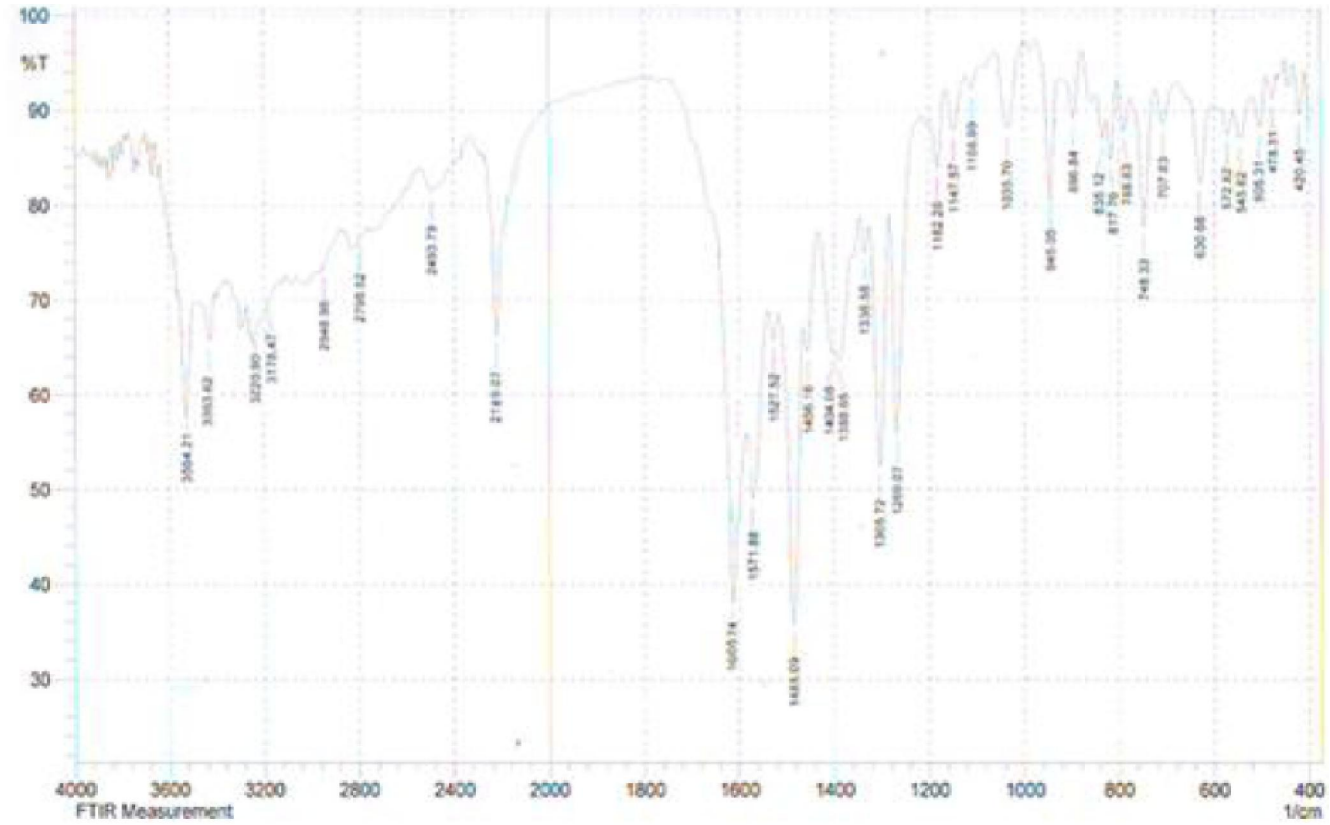


Figure 2 : FTIR spectrum of L_2

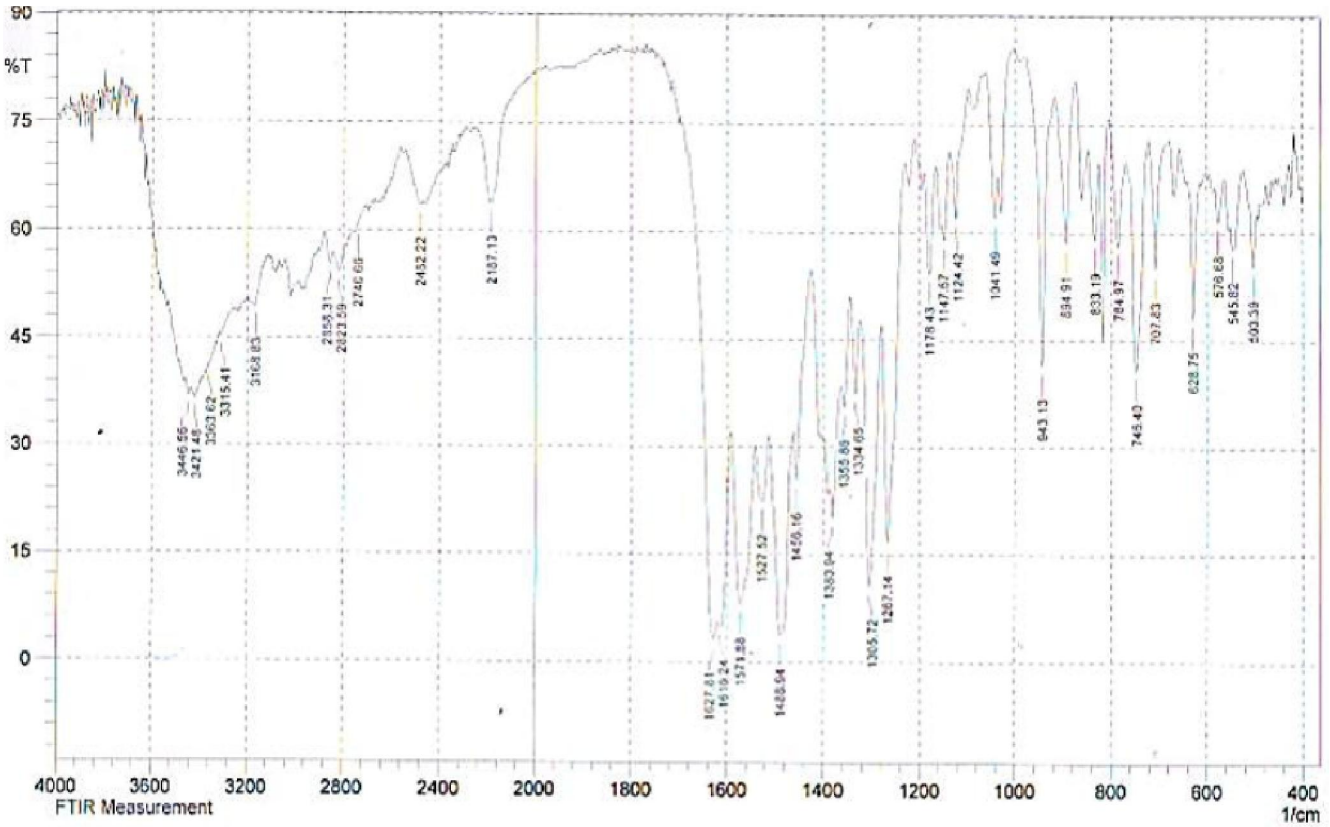


Figure 3 : FTIR spectrum of C_1

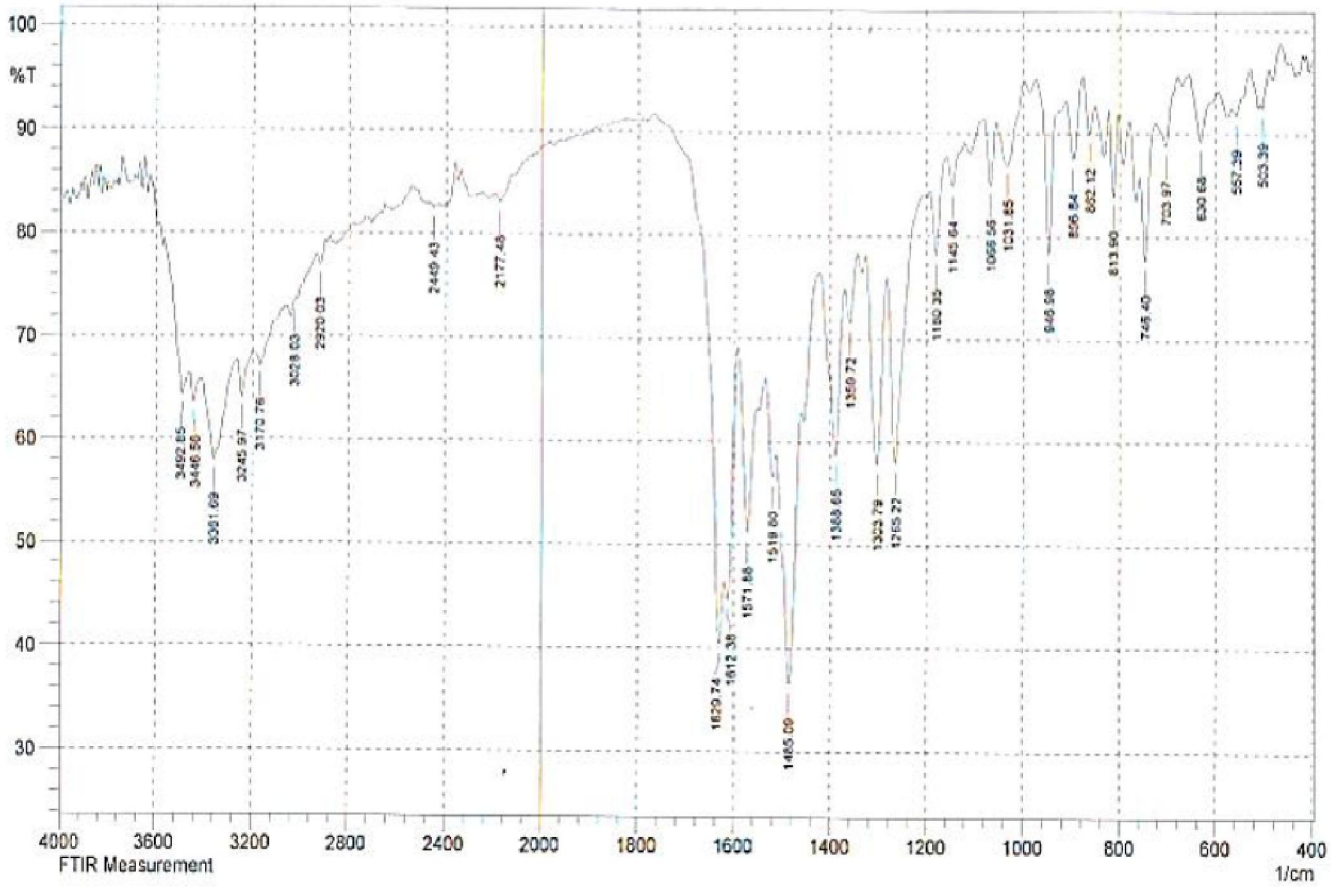


Figure 4 : FTIR spectrum of C_2

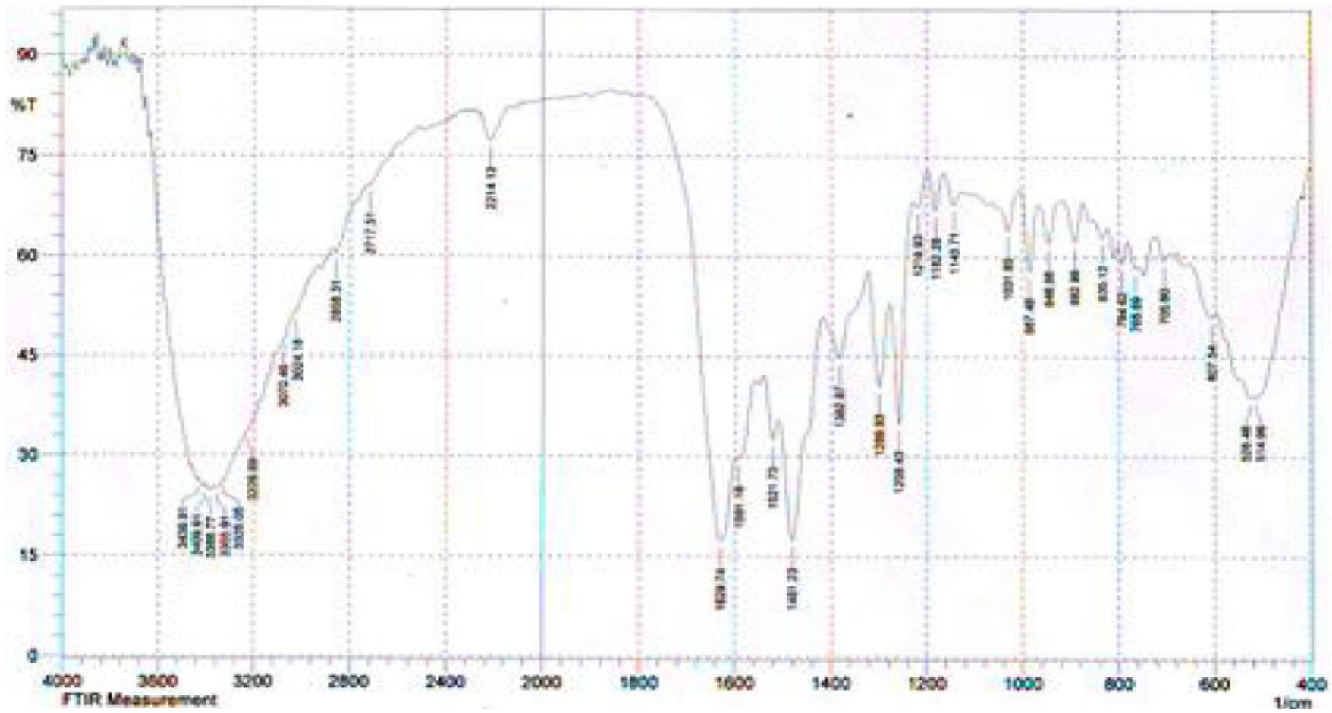


Figure 5 : FTIR spectrum of C_3

the most important stretching modes exhibited by (L_2) were represented by α-amino and nitrile groups. The

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

Comp.	Formula	Groups	Chemical Shifts δ(ppm)
L_1	$C_{17}H_{21}FClN_3O_4$	(-C<u>H</u>$_2$-)	1.42
		(=NH)	2.22
		(-C<u>H</u>$_2$-N=)	3.46
		(Ar-<u>H</u>)	7.45-7.55
		(-COO<u>H</u>)	8.92
L_2	$C_{18}H_{14}N_2$	(=N<u>H</u>)	3.79
		(=CH-C=N)	5.45
		(Ar-<u>H</u>)	6.79-7.92
C_1	$[MnL_1L_2Cl(H_2O)].2H_2O$	(=NH)	3.41
		(=C<u>H</u>-C=N)	5.34
		(Ar-H)	6.31-7.56
		(-COO<u>H</u>)	8.72
C_2	$[CuL_1L_2(H_2O)_2]Cl.2H_2O$	(=NH)	3.53
		(=C<u>H</u>-C=N)	5.82
		(Ar-H)	6.82-7.97
		(-COO<u>H</u>)	8.71
C_3	$[CrL_1L_2Cl(H_2O)]Cl.3H_2O$	(=NH)	3.98
		(=C<u>H</u>-C=N)	5.53
		(Ar-H)	6.21-7.98
		(-COO<u>H</u>)	8.70

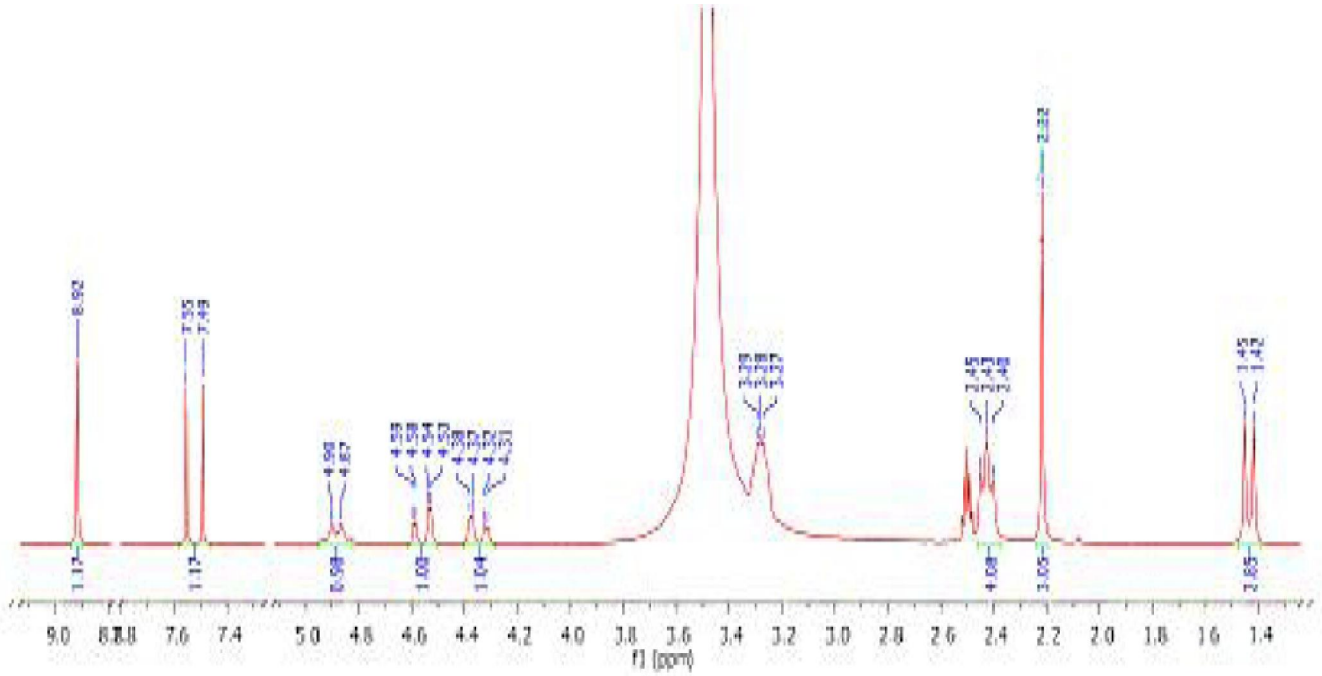

Figure 6 : ^{1}H-NMR spectrum of L_1

bands assigned to stretching vibration of aromatic and aliphatic (C-H) of the two ligands appeared at (3000-3170) cm^{-1} and (2850-3000) cm^{-1} respectively[9,10]. The band related to υ(C≡N) stretching vibration of the free ligand appeared at (2189cm^{-1})[11,12]. The band related to υ(N-H) stretching vibrations appeared at (3363 cm^{-1})[13,14]. The band related to υ (N-H) bending vibration appeared at (1605 cm^{-1})[15,17].

Complexes (C_1-C_3)

The FTIR spectral data of the complexes were shown in TABLE (2) and their spectra were shown in Figures (3, 4 and 5).

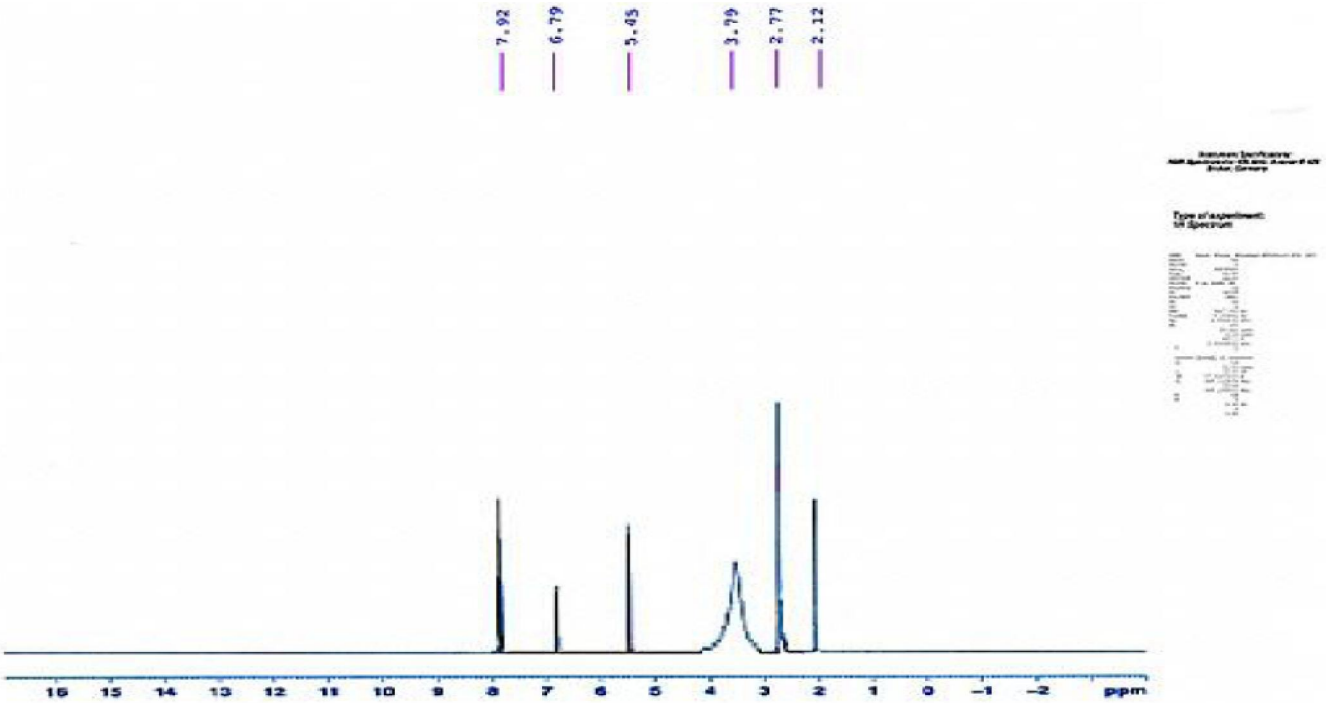

Figure 7 : ^{1}H-NMR spectrum of L_2

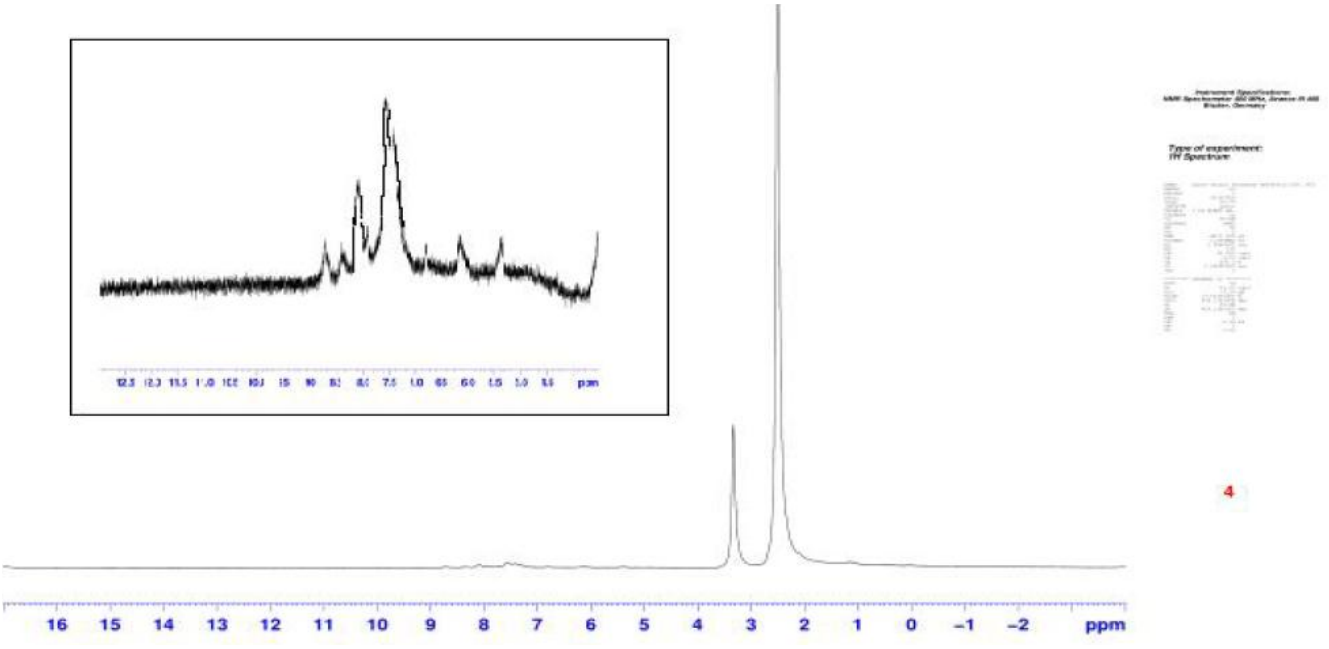

Figure 8 : ^{1}H-NMR spectrum of C_1

The spectra of the complexes exhibited characteristic bands of either coordinated water appeared at (3450-3531) cm^{-1} assigned to υ(OH) in the complexes C_1 and C_3 or lattice water appeared at (746 cm^{-1}) assigned to ρw (H_2O) in C_2 complexe[18,19]. The band at (3363 cm^{-1}) which was assigned to the υ(N-H) stretching vibration of the (N-H) group of (L_2) was shifted in the spectra of complexes (C_1, C_2 and C_3) to (3315, 3351 and 3385) cm^{-1} respectively. This gave an indication that the ligand was coordinated with the metal ions through the nitrogen atom of α-amino group. The band at (2189) cm^{-1} which was assigned to the stretching vibration of υ(C≡N) group of (L_2) was shifted in the spectra of complexes (C_1-C_2) to lower frequencies (2157 and 2177) cm^{-1} respectively which refers to the linkage of (C≡N) group

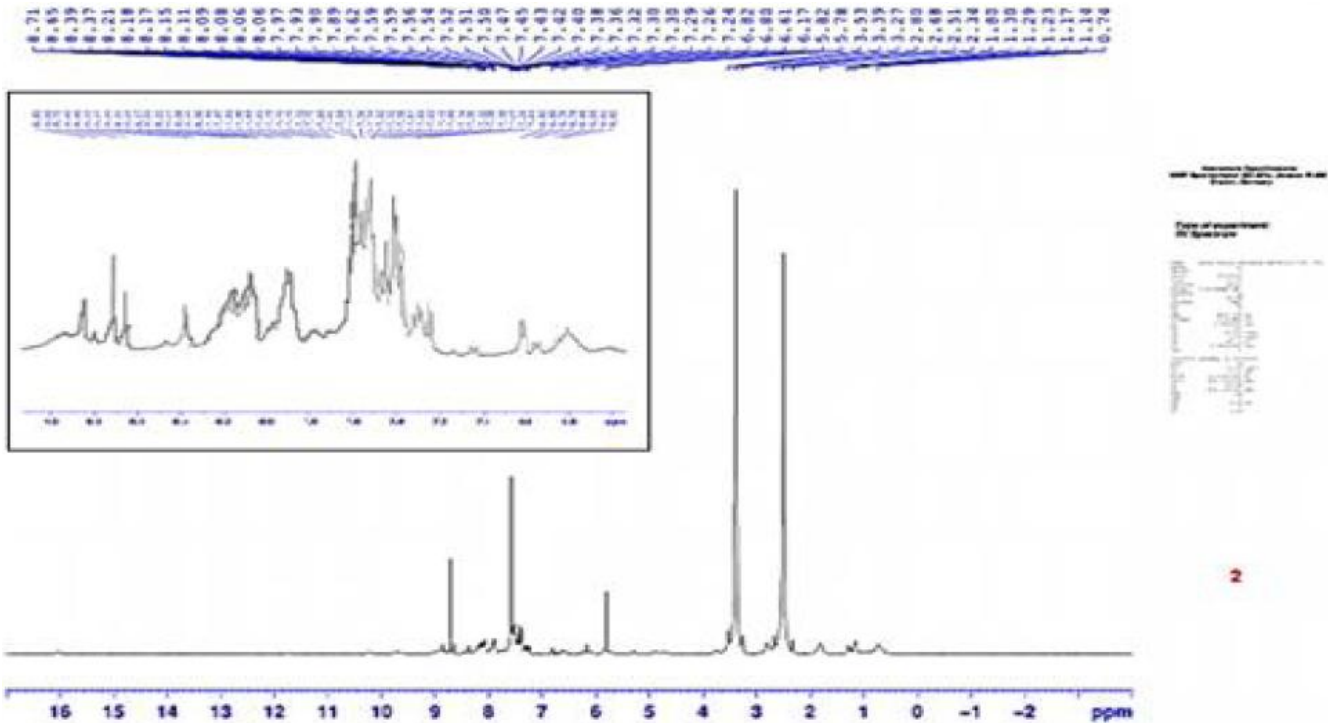

Figure 9 : ^{1}H-NMR spectrum of C_2

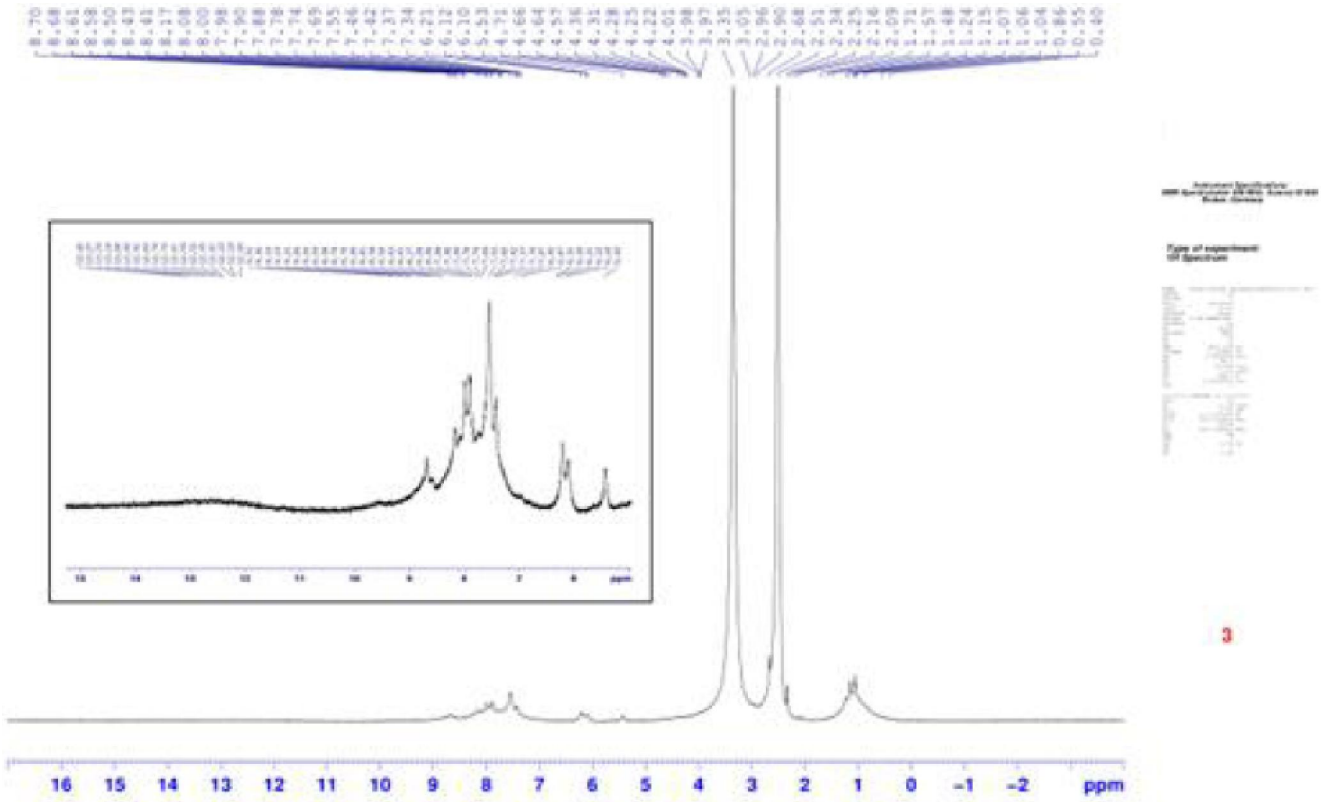

Figure 10 : ^{1}H-NMR spectrum of C_3

from nitrogen atom. The spectrum of complex (C_3) showed an increased shift in υ(C≡N) stretching vibration towards to higher frequency as a result of coordination with metal ion through the lone pair electrons of nitrogen atom. The decreases of υ(C≡N) stretching vibration of complexes (C_1-C_2) were at-

TABLE 4 : ^{13}C-NMR of the ligands(L_1, L_2 and L_3) and some of their metal ion complexes

Comp.	Formula	Groups	Chemical Shifts δ(ppm)
L_1	$C_{17}H_{21}FClN_3O_4$	$(-CH_2-CH_2-)$	7.7
		(=CH-N=)	35.8
		$(-CH_2-NH-)$	45.8
		$(CH_2-N=)$	51.3
		(COOH)	166.2
		(=C=O)	176.4
		Ar-H	115-102
L_2	$C_{18}H_{14}N_2$	(-CH-C=N)	53.20
		(-CH-C=N)	115.37
C_1	$[MnL_1L_2Cl(H_2O)].2H_2O$	(=CH-C=N)	51.39
		(-CH-C=N)	113.26
		(-COOH)	166.61
		(=C=O)	176.26
C_2	$[CuL_1L_2Cl(H_2O)_2].2H_2O$	(-CH-C=N)	57.68
		(-CH-C=N)	119.95
		(-COOH)	165.68
		(=C=O)	175.91
C_3	$[CrL_1L_2Cl(H_2O)]Cl.3H_2O$	(-CH-C=N)	53.13
		(-CH-C=N)	117.03
		(-COOH)	167.47
		(=C=O)	177.26

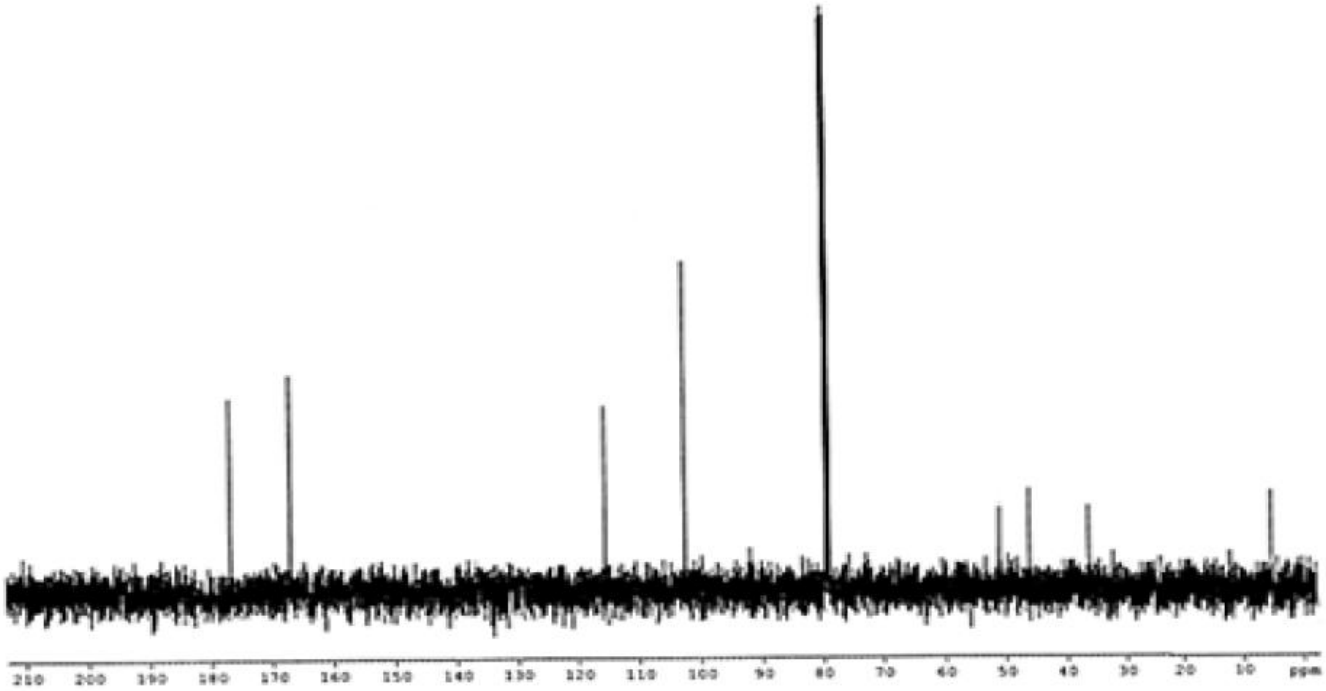

Figure 11 : ^{13}C-NMR spectrum of L_1

tributed to metal dπ to ligand pπ* back- bonding. But the increase of υ(C≡N) stretching vibration of complex (C_3) attributed to presence of ΐ accepter ligand into complex (C_3) should decrease the back bonding of electrons from the metal into the nitrile ligand. The band at (1605)cm^{-1} which was assigned to the υ(N-H) bending vibration of (N-H) group of (L_2) was shifted in the spectra of complexes (C_1, C_2 and C_3) to (1627, 1629 and 1629) cm^{-1} respectively, this gave further indication that the ligand was coordinated with metal ions through the nitrogen atom of α-amino group and thus supports the complexes formation. The band at (1706 cm^{-1}) which was assigned to the υ(C=O) stretching vibration of the carboxylic

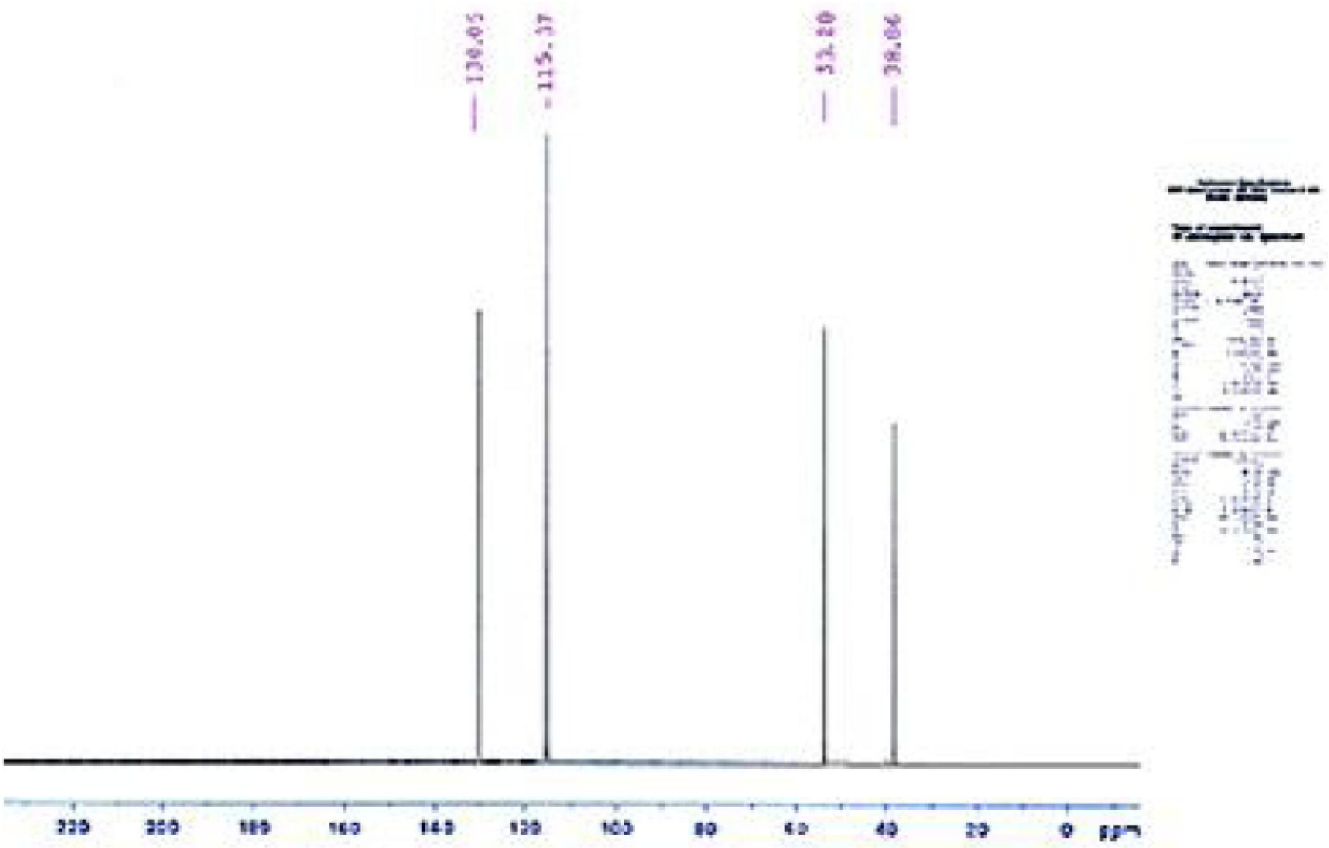

Figure 12 : ^{13}C-NMR spectrum of L_2

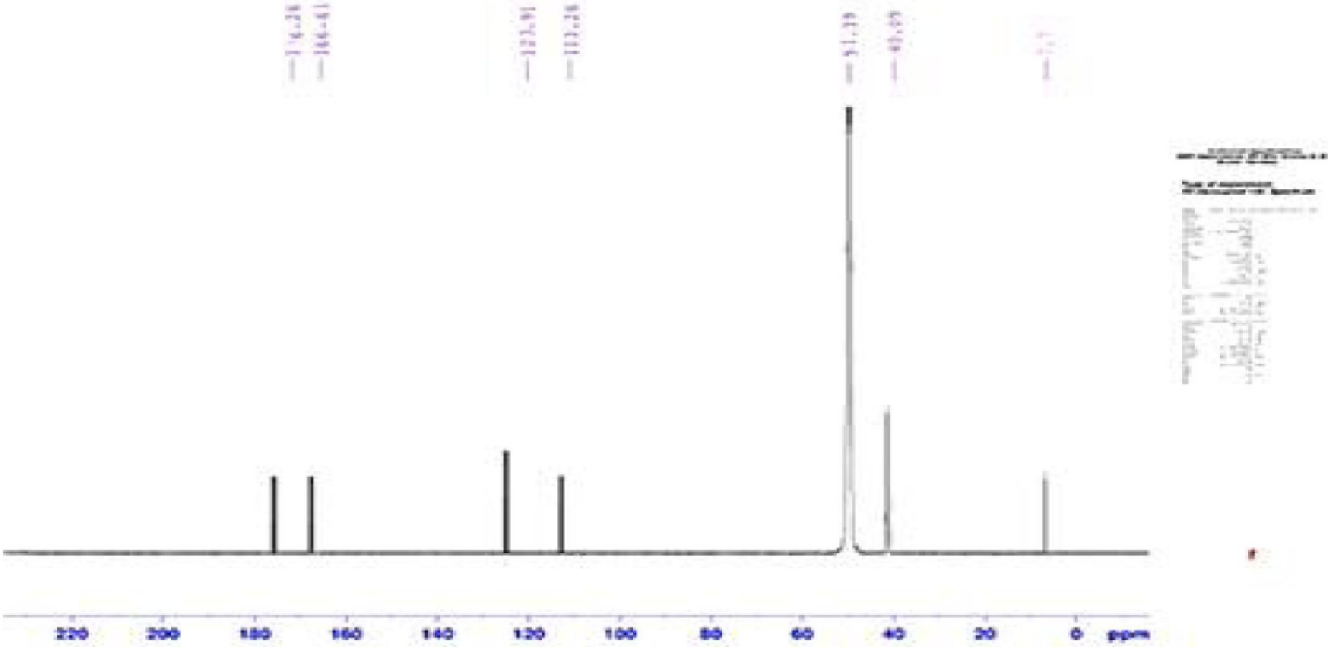

Figure 13 : ^{13}C-NMR spectrum of C_1

group (L_1) in addition, ionic carboxylic have two absorption bands in the ranges (1510-1600) cm^{-1} and (1257-1400) cm^{-1}, which could be assigned to υ(C-O-C) asymmetric and symmetric was shifted in the spectra of stretching vibration respectively[20]. The absorption bands spread around (1494) cm^{-1}, corresponding to the stretching vibrations of C–C and C–N bonds in quinolone ring. Coordinated by two

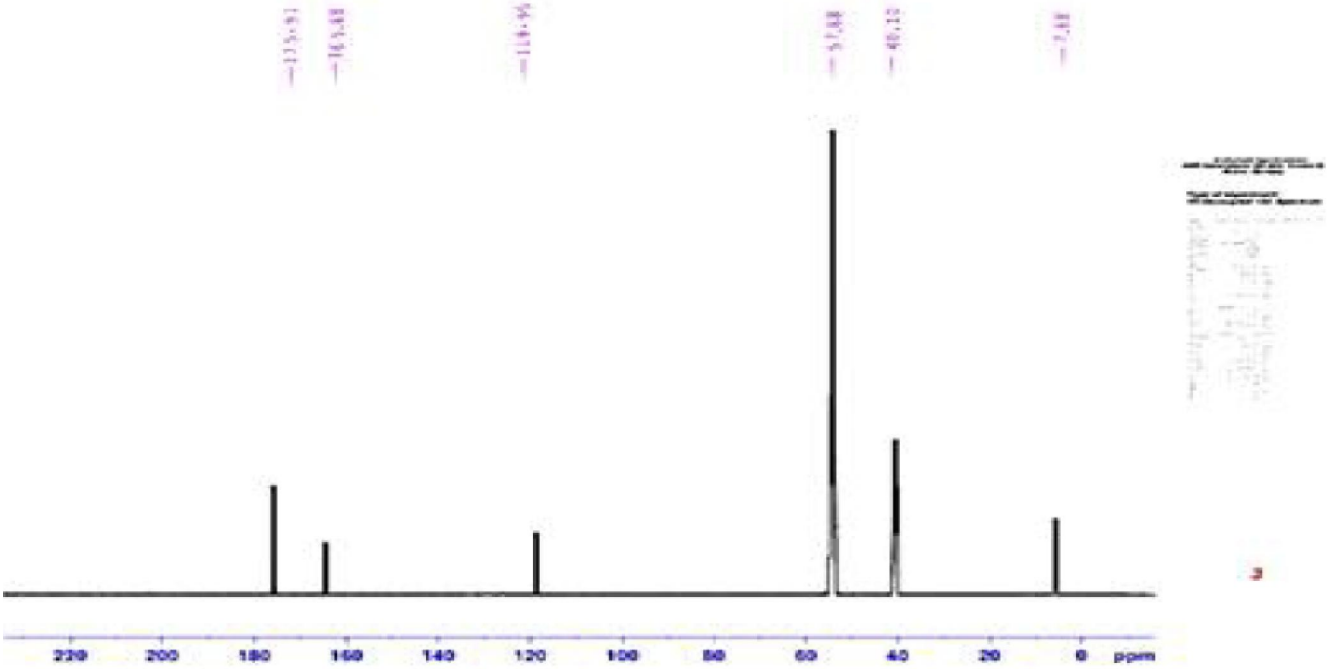

Figure 14 : [13] C-NMR spectrum of C_2

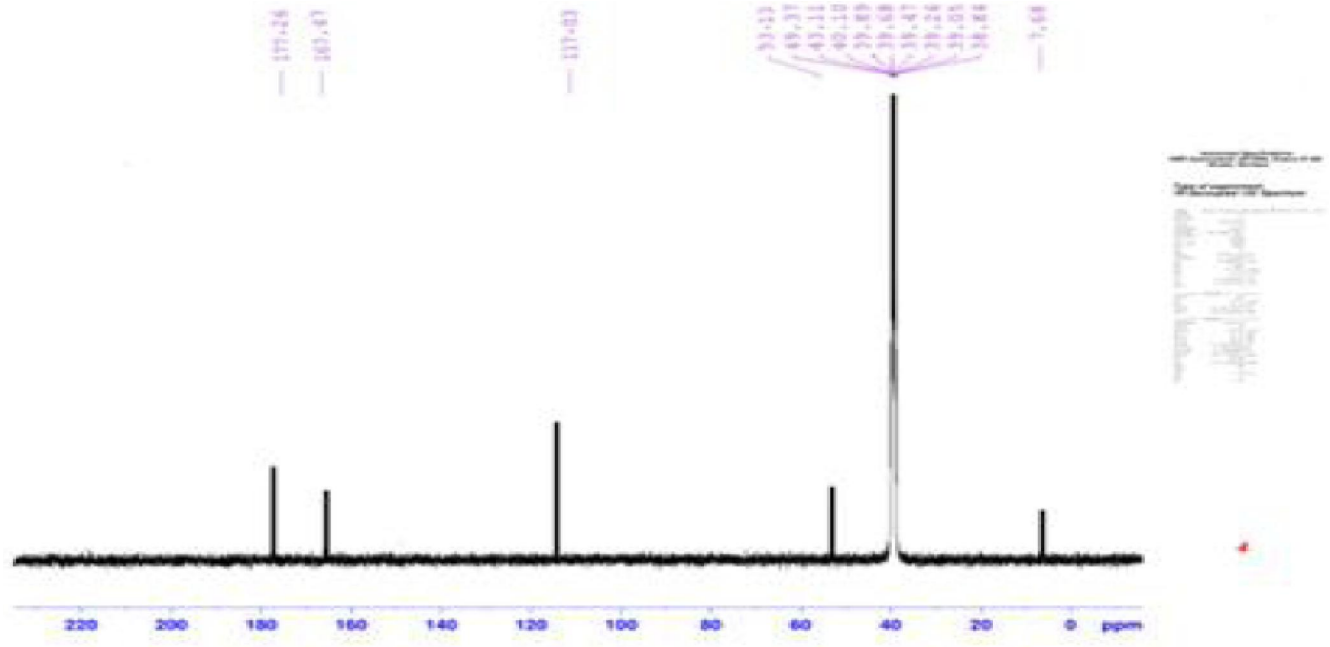

Figure 15 : [13] C-NMR spectrum of C_3

oxygen atoms from quinolone molecules (one oxygen from pyridine and one from the carboxylic group)[22]. New bands appear in the region (514-557) cm-[1] assigned to υ(M-N) and New bands appear in the region (428-480) cm-[1] assigned to υ(M-O)[20].

[1]H-NMR AND [13]C-NMR SPECTRA

[1]H-NMR

The two ligands (L_1 and L_2) were characterized by [1]H-NMR and [13]C-NMR spectroscopic methods, in addition to three complexes (C_1, C_2 and C_3) using DMSO (d6) as shown in TABLE (3) and Figures (6-10).

The [1]H-NMR spectra of the ligand (L_1) showed five peaks; the first one appeared at δ)1.42) ppm which was assigned to the (-C<u>H</u>$_2$-), the second peak appeared at δ(2.22) ppm was assigned to the (=N<u>H</u>)

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TABLE 5 : Electronic spectra, parameter, molar conductance, magnetic susceptibility and suggested stereo chemical of ligand and their metal ion complexes

Comp.	Wavelength(nm)λ	wave no. ύ(cm)$^{-1}$	Assignment	Molar Cond. Ω^{-1} cm^2 mol^{-1}	B cm^{-1}	β	^{1}cm 15B	(B.M)	Geometry Suggested
L_1	316	31645	$n\rightarrow\pi^*$	------	----	----	----	----	--------
	280	35714	$\pi\rightarrow\pi^*$						
L_2	361	27700	$n\rightarrow\pi^*$	------	----	----	----	----	--------
	290	34482	$\pi\rightarrow\pi^*$						
C_1	532	18797	$^6A_1g\rightarrow{}^4T_1g$	21.2	----	----	----	1.94	Octahedral
C_2	489	20450	$^2E\ g\rightarrow{}^2T_2\ g$	38.3	----	----	----	1.87	Distorted Octahedral
	----	13430(cal)	$^4A_2g\rightarrow{}^4T_2g$						
C_3	632	15822	$^4A_2g\rightarrow{}^4T_1g_{(F)}$	45.6	771	0.840	11566	3.14	Octahedral
	445	22471	$^4A_2g\rightarrow{}^4T_1g_{(P)}$						

cal.=calculated value

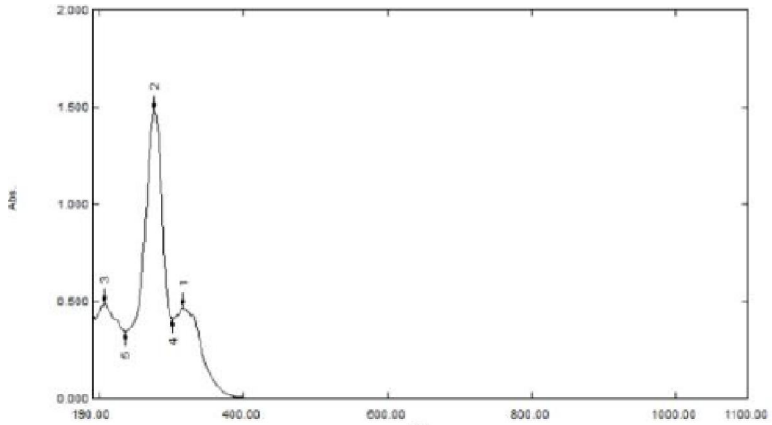


Figure 16 : UV-Visible Spectrum of L_1

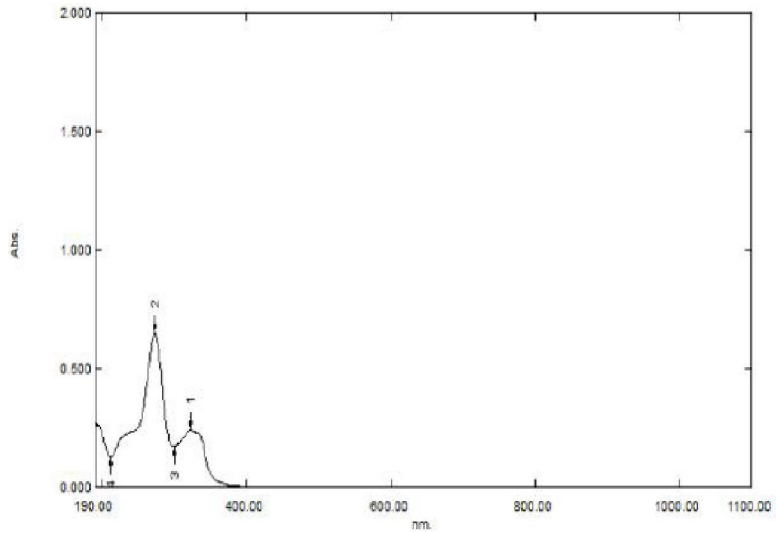


Figure 17 : UV-Visible Spectrum of L_2

proton while the third peak appeared at δ)3.46) ppm which was corresponded to the (-C$\underline{H}_2$-N=)[21]. The forth peak appeared at δ(7.45-7.55) ppm was attributed to the aromatic protons and the last one appeared at δ)8.92) ppm assigned to the (-COO$\underline{H}$)[22].

The ^{1}H-NMR spectra of the ligand (L_2) showed four peaks; the first one appeared at at δ)2.77) ppm which was assigned to the solvent peak (DMSO),

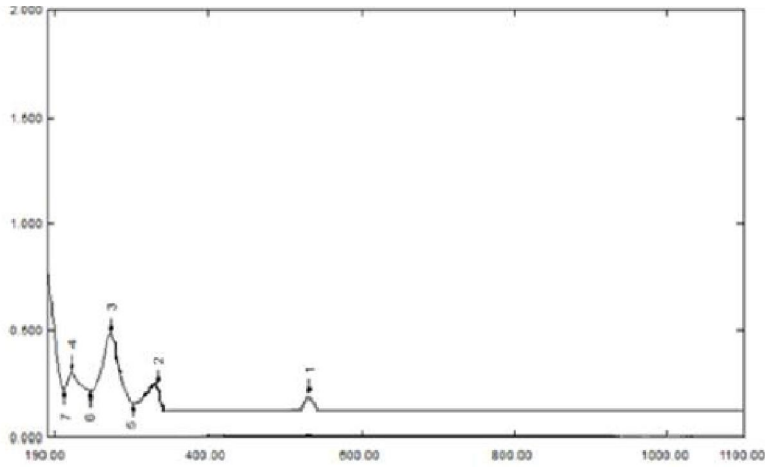


Figure 18 : UV-Visible Spectrum of C_1

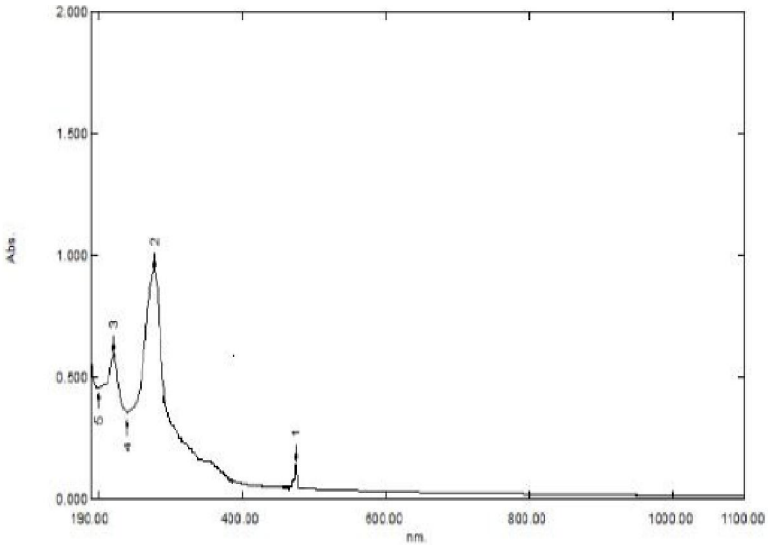


Figure 19 : UV-Visible Spectrum of C_2

the second peak appeared at δ(3.79) ppm was assigned to the (-N-_H) proton while the third peak appeared at δ(5.45) ppm which was corresponded to the (-CHC≡N). The last peak which appeared at δ(6.79-7.92) ppm was attributed to the aromatic protons[23].

The ^{1}H-NMR spectra of the complexes (C_1, C_2 and C_3) were similar to that of the ligands, the only three difference were that the signal of (=N-_H) of the ligand was shifted in these complexes by (0.12, 0.19 and 0.38) ppm respectively and the signal of (-CH-C≡N) was shifted in these complexes by (0.22, 0.08 and 0.11) ppm and the last signal of (-COOH) was shifted by (0.73, 0.22 and 0.20) respectively, this gave an indication for complexes formation.

^{13}C-NMR Spectra

The two ligands (L_1 and L_2) were characterized by ^{13}C-NMR spectroscopic methods, in addition to three complexes (C_1, C_2 and C_3) using DMSO (d6) as shown in TABLE (4) and Figures (11-15).

The ^{13}C-NMR spectrum of the ligand (L_1) showed seven peaks; the first peak appeared at δ(7.7) ppm which was corresponded to the (-CH_2-CH_2-). The second peak appeared at δ(35.8) ppm was corresponded to the (=_CH-N=) carbon, the third peak appeared at δ(45.8) ppm was assigned to the (-_CH_2-NH-) carbon, the forth peak appeared at δ(51.3) ppm was assigned to the (-_CH_2-N=) carbon, the fifth peak appeared at δ(166.2) ppm which was assigned to the (-_COOH) carbon, the sixth peak appeared at δ(176.4) ppm was assigned to the (=_C=O) carbon, and the last peak appeared at δ (102-115) ppm was assigned to the aromatic carbon atoms[21].

Full Paper

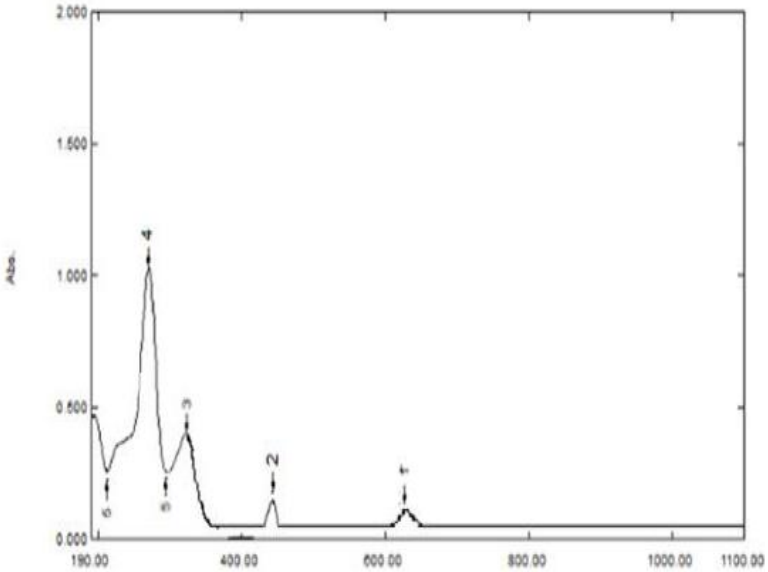


Figure 20 : UV-Visible Spectrum of C_3

TABLE 6 : Inhibition zones measured in (mm) of DMSO, ciprofloxacin and complexes

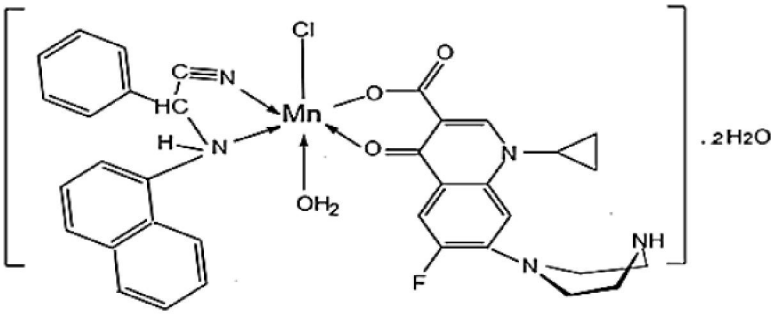
Compound	Inhibition zone (mm) Escherichia coli	Inhibition zone (mm) Pseudomonas aeruginosa	Inhibition zone (mm) Staphylococcus aureus	Inhibition zone (mm) Streptococci
DMSO	----	----	----	----
L_1(ciprofloxacin)	18.5	23.7	18.1	12.2
C_1	9.0	16.6	7.5	12.1
C_2	8.5	42.5	5.5	14.3
C_3	20.1	42.3	23	19.4

The ^{13}C-NMR spectrum of the ligand (L_2) showed three character peaks; the first peak appeared at δ(38.86) ppm which was corresponded to the solvent peak (DMSO), the second peak appeared at δ((53.20ppm which was corresponded to the (-_CH-C≡N) carbon and the last peak appeared at δ((115.37 ppm was assigned to the (-CH-_C≡N) carbon atom[22].

The ^{13}C-NMR spectra of the complexes (C_1, C_2 and C_3) were similar to that of the ligands, the only difference was that the signal of (-NH-_CH-C≡N) carbon of the ligand was shifted in these complexes by (1.81, 4.48 and 0.07) ppm respectively, the signal of (-CH-_C≡N) carbon was shifted in these complexes by (2.11, 4.58 and 1.83) ppm and the signal of (-_C=O) carbon was shifted in these complexes by (0.4, 0.52 and 1.27) ppm and the signal of (-_COOH) carbon was shifted in these complexes by (0.14, 0.49 and 0.86) ppm respectively, this gave an indication for complexes formation[23].

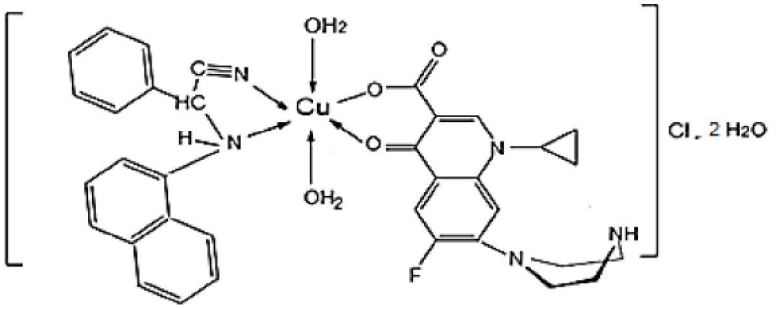
ELECTRONIC SPECTRA (UV-VIS.)

The electronic absorption data of the ligands (L_1 and L_2) and their complexes were recorded in ethanol at room temperature were shown in TABLE (3), while their spectra were shown in Figures (16-20). The spectra of two ligands exhibited a high intensity band appeared in the region (48543and 34482) cm^{-1} respectively assigned to $\pi \rightarrow \pi^*$ of conjugated system[24]. Low intensity bands appeared in the near UV. region (31645 and 27700) cm^{-1} respectively, were assigned to $n \rightarrow \pi^*$ transition, the intensity and positions of these bands depends on the structure of molecules and the nature of the solvent used[25]. The electronic spectra of the complexes exhibited of new bands, the intensities and positions of these bands are mainly dependent on the ligand field effects, stereochemistry of complexes and electron configuration of the metal ions[26].



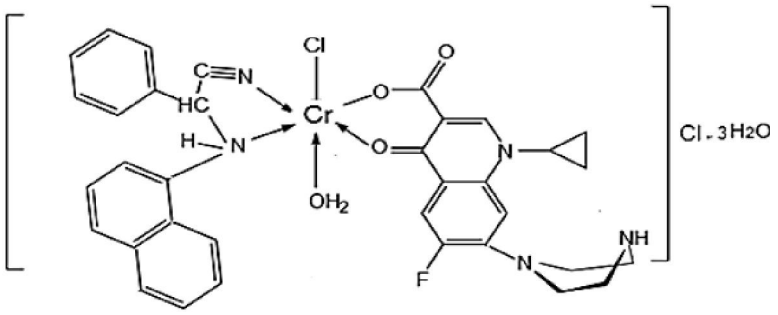
[Mn $L_1L_2Cl(H_2O)$].$2H_2O$
[chloro mono aqua ciprofloxacin {2-phenyl-2-(1-Naphthylamine) acetonitrile} nickel(II)] dehydrate

Figure 21 : Suggested structure of C_1



[$CuL_1L_2(H_2O)_2$]Cl.$2H_2O$
[di aqua ciprofloxacin {2-phenyl-2-(1-Naphthylamine) acetonitrile} copper(II)] dehydrate

Figure 22 : Suggested structure of C_2



[$CrL_1L_2Cl(H_2O)$]Cl.$2H_2O$
[chloro mono aqua ciprofloxacin {2-phenyl-2-(1-Naphthylamine) acetonitrile} chrome(III)] chloride (3)hydrate

Figure 23 : Suggested structure of C_3

In vetro antibacterial activity

The antibacterial activities of all complexes were screened against test bacteria namely; *Staphylococcuaurouss, Bacillus subtilis* (Gram+), *Escherichia* and *Pseudomonas aerugin* (Gram-). Agar, (well-diffusion method) used to determine the activity[27]. Borer of 0.6 mm diameter was used, the concentration of all complexes is (10^{-3}M) using (DMSO) was a solvent and was used as a control Gram negative while ciprofloxacin was used as a control Gram positive. The solvent (DMSO) showed no activity against the tested bacteria, while some of prepared complexes showed very good results[28]. TABLE (6) shows the inhibition zones of the solvent and the prepared complexes. The inhibition zones were measured in (mm) and compared to the inhibition zone of broad spectrum antibiotic. All complexes showed no activity against the gram negative bacterium (*Escherichia coli*), which can cause disease, for example, enter toxigenic strains produce a toxin in the gut, resulting typically in diarrhea[29]. The complexes (C_2 and C_3) showed highest activity against *Pseudomonas*. This bacterium is known for its resistance to most of the developed antibiotics

and is known to be the major case of many health issues and infections[30]. Many factors were reported to control the biological activities of metal complexes[31].

Type of ligand, type of metal, charge of complex, the transition series, configuration of metal ion and geometry of metal complex are effected on biological Activity[32].

The nomenclature of suggested structures of the complexes

The suggested structures of prepared complexes were confirmed by their element analysis (C.H.N.), thermal analysis, infrared, ^{1}H-NMR and ^{13}C-NMR spectra, UV-Visible spectroscopy, also by molar conductance values. According to the observation obtained the structures of complexes are suggested as illustrated in figures below:

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