ISSN: 0067-2904
GIF: 0.851

Synthesis and Characterization of Some New Metal Complexes of 2-phenyl-2-(p-tolylamino) and 2-phenyl-2-(phenylamino) Acetonitrile Compounds

Mohammed H. A. Al-Amery , Hamid Sattar Meteab*
Department of Chemistry, College of Science, University of Baghdad, Baghdad, Iraq.

Abstract:

The synthesis and characterization of new complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) with bidentate [L_1: 2-phenyl-2-(p-tolylamino) acetonitrile] and [L_2: 2-phenyl-2-(phenylamino) acetonitrile] ligands has been described. The two ligands were prepared by the reaction of p-toluidine and aniline with benzaldehyde, respectively in the presence of potassium cyanide and acidic medium. The complexes were synthesized by treating an ethanolic solution of the ligand with metal salts in a mole ratio of [1:2] [M:L]. The complexes were characterized by using metal and elemental analyses, electronic spectra, ^{1}H-NMR, ^{13}C-NMR, Thermal Gravimetric Analysis TGA, molar conductivity and magnetic susceptibility. According to the obtained data the probable coordination geometries of metal ions in these complexes were suggested as octahedral. Some complexes were found to be non-electrolyte others were found to be weak electrolyte in ethanol.

Keywords: 2-phenyl-2-(phenylamino) acetonitrile, Transition metal ions

تحضير وتشخيص بعض المعقدات الجديدة لمركبات [2-فنيل-2-(بارا- توليلامينو) و2-فنيل-2-(فنيل امينو)] اسيتونتريل

محمد حسين عباس العامري، حامد ستار متعب*
قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة:

تضمنت هذه الدراسة تحضير وتشخيص معقدات جديدة ل Cr(III)، Fe(III) ، Co(II)، Ni(II)، Cu(II)، Zn(II) مع ليكاندين ثنائية السن [2-فنيل-2-(بارا- توليلامينو) و2-فنيل-2-(فنيل امينو) اسيتونتريل] اللذين تم تحضيرهما من تفاعل الباراتوليودين والانيلين مع البنزلدهايد على التوالي بوجود KCN في محيط حامضي. حضرت المعقدات من خلال معاملة الليكاند مع املاح العناصر بنسبة مولية [2:1] [ملح:ليكاند]. شخصت المعقدات من خلال التحليل الدقيق للعناصر و مطيافية الامتصاص الذري و اطياف الاشعة تحت الحمراء و بروتون الرنين النووي المغناطيسي ونظير الكاربون13 للرنين النووي المغناطيسي والتحليل الحراري الوزني و التوصيلية المولارية والحساسية المغناطيسية. طبقآ للبيانات التي تم الحصول عليها تم اقتراح الاشكال الهندسية المحتملة لهذه المعقدات على انها ثمانية السطوح. بعض المعقدات وجدت غير الكتروليتية والبعض الآخر وجدت بشكل الكتروليت ضعيف في الايثانول.

---

*Email: Hamid Algarah@Yahoo.Com

Introduction:

α-Aminonitriles are a class of compounds which contain amine and nitrile functional groups on the same carbon atom [1]. α-Aminonitriles can be easily synthesized from aldehydes or ketones by the Strecker synthesis, which is an efficient one step synthesis involving the use of sodium cyanide and ammonium chloride in water. Primary or secondary amine salts can also be used to synthesize α-aminonitriles [2]. α-Aminonitriles are important synthetic intermediates for preparing of α-amino acids and nitrogen-containing heterocyclic [3]. α-Aminonitrile compounds are well known to be biologically active species in pharmaceutical, biocatalysts and industry [4,5]. Some α-aminonitriles contain additional donor atoms and hence act as good chelating agent with different metal ions [6, 7]. In this work the preparation of two α-aminonitrile bidentate legands (L_1 and L_2) have been investigated as chelating agents with some transition metal ions such as [Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II)] . The two ligands and their complexes were characterized by metal and elemental analyses, electronic spectra, ^{1}H-NMR, ^{13}C-NMR, Thermal Gravimetric Analysis TGA, molar conductivity and magnetic susceptibility.

Experimental:

1. Chemicals:

All the following chemicals and reagents were of analytical grade and were used as supplied without any further purification. Metal salts $CrCl_3.6H_2O$, $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ and $ZnCl_2$ (BDH), $FeCl_3.6H_2O$ (Merck), $NiCl_2.6H_2O$ (Analar). Benzaldehyde, aniline, p-toludine, glacial acetic acid, potassium cyanide (BDH), ethanol, absolute ethanol (Fluka), petroleum ether (30-60) (SCR- China) and HCl (Loba Chemie-India).

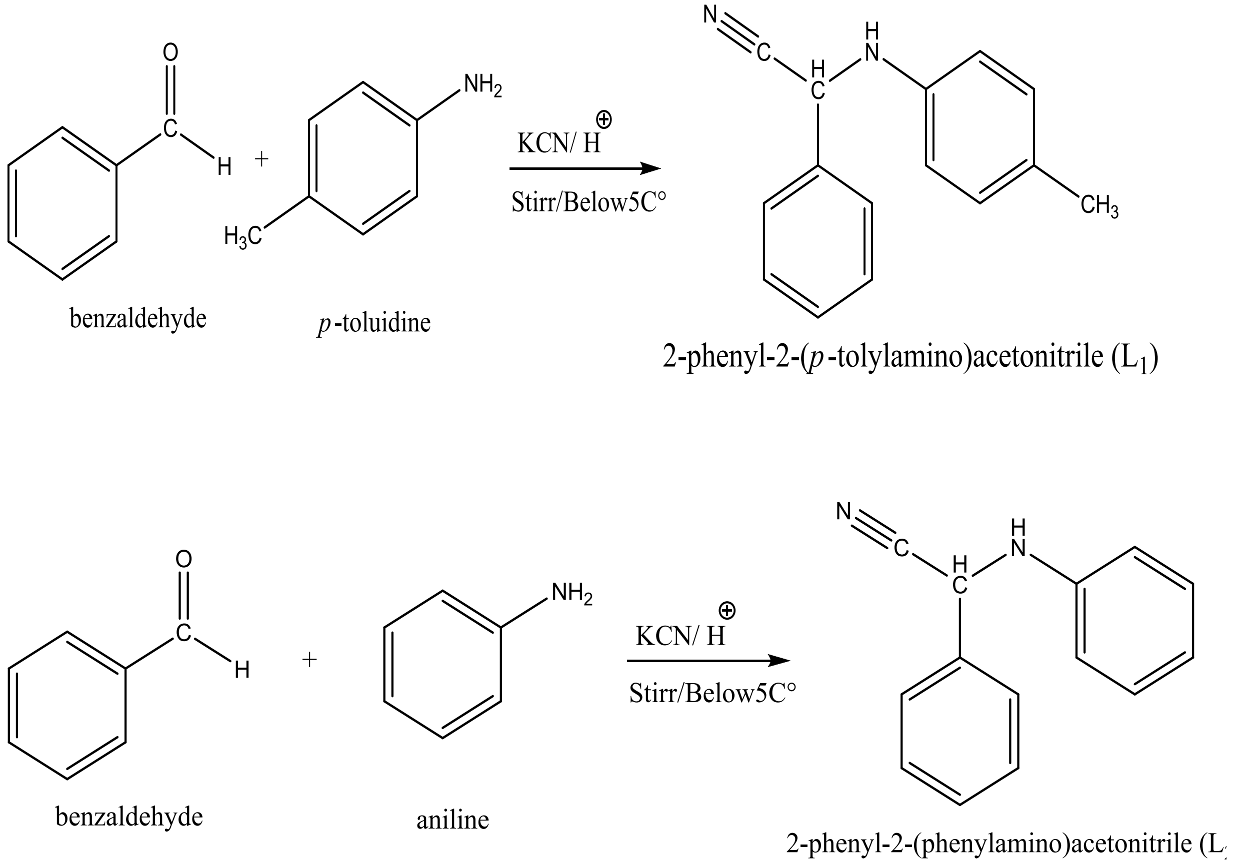
2. Instruments:

The infrared spectra of the ligands and the complexes were recorded on SHIMADZU 8300 FTIR Spectrophotometer as KBr disk. Electronic absorption spectra were recorded on SHIMADZU 1800-UV. Atomic Absorption technique was used to determine the metal contents of the complexes using Phoenix-986 Spectrophotometer. Molar conductivity was used to measure the conductivity of the complexes (10^{-3} M) at room temperature in ethanol using (CDM 83) Digital conductivity meter. Elemental analysis for carbon, hydrogen and nitrogen elements; were performed by using Euro: (EA) Elemental analyzer. ^{1}H-NMR and ^{13}C-NMR Spectra of the ligands and their complexes were recorded in DMSO using (Avance III Broker) 400 MHZ NMR Spectrometer, Germany. Thermal Gravmetric Analyses (TGA) was recorded on SETARAM D350 analyzer. The magnetic properties were measured by using Auto Magnetic susceptibility Balance (Sherwood Scientific). Melting point was measured using a Stuart SMP30 Digital Melting Point apparatus.

Preparation of ligands:

The two ligands were prepared by following a previously reported method except changing of primary aromatic amine (aniline and P-toluidine) [8].

Potassium cyanide (1.30 gm, 2mmole) was dissolved in distilled water (4 ml) and cooled below 5°C. To this solution, benzaldehyde (2.12 gm, 2mmol) in ethanol (25ml, 95%) was added. The mixture was stirred maintaining temperature below 5°C. To this mixture glacial acetic acid (1.20 gm, 2mmol) was added with constant stirring below 5°C, aniline (1.86 gm 2mmol) or p-toluidine (2.14 gm 2mmol) in (10ml 95%) ethanol and (5ml) of acetic acid (cooled below 5°C) was added with continuous stirring in well ventilated hood. Temperature was maintained at 15°C during addition. The reaction mixture was stirred for further 2 hrs and was kept at room temperature (25°C) for 24 hrs. The obtained long (yellow and light brown) needles were washed with diluted hydrochloric acid (0.2M) to remove any excess of cyanide. The compounds were recrystallized with 95% ethanol. The synthesis routes of the two ligands are illustrated in scheme 1.



Scheme 1-Synthesis of α-aminonitrile L_1 and L_2

Preparation of Complexes:

a- Preparation of [L_1] Complexes (C_1- C_6)

A solution of (0.444gm, 2mmol) of ligand (L_1) in (10 ml) of absolute ethanol was added drop wise to a solution of (0.266gm, 0.27gm, 0.238gm, 0.237gm, 0.170gm and 0.136gm) respectively, of metal salts: ($CrCl_3.6H_2O$, $FeCl_3.6H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.6H_2O$ and $ZnCl_2$) respectively,(1mmol) in absolute ethanol with continuous stirring. The resulting mixture was refluxed at (75-85)°C for 4 hrs, and then the solution was left to be stirred overnight at room temperature. Gummy precipitates were formed. The products were treated with (30-60) petroleum ether for several times. The precipitates were collected and stored in desiccators. (Yield % of complexes C_1-C_6 = 83.9, 82.3, 75.5, 78.5, 84.6 and 75.0 respectively).

b- Preparation of [L_2] Complexes (C_7- C_{12})

The used procedure was similar to that which was described in section (a) expect the weight of ligand (L_2) was (0.416gm). (Yield % of complexes C_7-C_{12} = 85.4, 76.7, 79.1, 71.3, 82.8 and 77.2 respectively).

Results and Discussion:

Elemental analysis and some physical properties of the ligands (L_1, L_2) and their prepared complexes were shown in table 1.

Table 1- Elemental analysis and some physical properties of the ligands (L_1, L_2) and their prepared complexes

Comp.	Formula M.wt (gm/mol)	Yield %	Color	M.P. (°C)	C % Cal. (found)	H % Cal. (found)	N % Cal. (found)	M % Cal. (found)	Cl% Cal. (found)
L_1	$C_{15}H_{14}N_2$ (222.0)	86.9	Yellow	93-95	81.08 (80.49)	6.30 (6..15)	12.61 (12.44)	-----	-----
C_1	$[Co(L_1)_2Cl_2].2H_2O$ (609.0)	83.9	Gray	161-163	59.02 (58.74)	5.24 (4.90)	9.18 (8.64)	9.6 (9.4)	11.6 (11.1)
C_2	$[Cr(L_1)_2Cl_2]Cl.3H_2O$ (656.4)	82.3	Light Green	180-183	54.84 (54.26)	5.17 (4.76)	8.53 (8.07)	7.9 (7.3)	16.2 (15.5)
C_3	$[Cu(L_1)_2Cl(H_2O)]Cl.\ H_2O$ (614.5)	75.5	Gray	192-195	58.58 (57.02)	5.20 (4.98)	9.11 (8.89)	10.3 (9.5)	11.5 (10.8)
C_4	$[Ni\ (L_1)_2Cl_2].\ H_2O$ (591.7)	78.5	Green Yellow	155-157	60.84 (58.96)	5.07 (4.90)	9.46 (8.93)	9.9 (9.3)	11.9 (11.5)
C_5	$Zn(L_1)_2Cl_2]2H_2O$ (616.3)	84.6	Yellow Orange	168-170	58.41 (57.88)	5.19 (4.94)	9.08 (8.51)	10.5 (10.0)	11.5 (10.7)
C_6	$[Fe(L_1)_2Cl_2]Cl.2H_2O$ (642.3)	75.0	Sepia	199-201	56.04 (55.40)	4.98 (4.82)	8.71 (8.28)	8.6 (7.7)	16.5 (16.0)
L_2	$C_{14}H_{12}N_2$ (208.0)	78.5	Light Brown	75-77	80.76 (79.65)	5.76 (5.47)	13.46 (13.28)	-----	-----
C_7	$[Co(L_2)_2Cl_2]\ .3H_2O$ (599.9)	85.4	Gray	157-159	56.00 (55.46)	5.00 (4.58)	9.33 (8.79)	9.8 (9.5)	11.8 (11.1)
C_8	$[Cr(L_2)\ _2Cl_2]Cl.4H_2O$ (646.4)	76.7	Gray	191-193	51.98 (50.49)	4.95 (4.62)	8.66 (8.18)	8.0 (7.3)	16.4 (15.2)
C_9	$[Cu(L_2)_2Cl(H_2O)]Cl.1.5H_2O$ (595.5)	79.1	Gray	187-189	56.42 (55.66)	4.86 (4.37)	9.40 (8.78)	10.6 (10.0)	11.9 (11.1)
C_{10}	$[Ni(L_2)_2Cl_2.2H_2O$ (581.7)	71.3	Pine Green	163-165	57.76 (56.91)	4.81 (4.37)	9.62 (8.88)	10.0 (9.5)	12.2 (11.3)
C_{11}	$[Zn(L_2)_2Cl_2].3H_2O$ (606.3)	82.8	Light Yellow	172-175	55.41 (54.90)	4.94 (4.39)	9.23 (8.83)	10.7 (10.1)	11.7 (11.0)
C_{12}	$[Fe(L_2)_2Cl_2]Cl.3H_2O$ (632.3	77.2	Sepia	196-198	53.13 (52.72)	4.74 (4.35)	8.85 (8.18)	8.8 (7.5)	16.8 (15.9)

FTIR Spectra:

α-Aminonitrile ligands

The FTIR data of α-aminonitrile compounds (L_1 and L2) and their metal complexes are shown in table 2 and the IR spectra of some complexes were illustrated in figures 1 and 2. The bands assigned to stretching vibrations of aromatic and aliphatic (C-H) of the two ligands appeared at (3150-3000) and (3000-2850) cm^{-1} respectively [9, 10]. The bands related to υ(C≡N) stretching vibrations of the free ligands appeared at (2241 and 2250) cm^{-1} respectively [11, 12]. The bands related to (N-H) stretching vibrations appeared at (3329 and 3337) cm^{-1} [13-15] respectively. The bands related to (N-H) deformation appeared at (1601 and 1616) cm^{-1} respectively [16, 17].

Complexes

The FTIR data of the complexes are described in table 2.The band assigned to the υ(N-H) stretching vibration of the (NH) group of (L_1) ligand was shifted in the spectra of the complexes (C_1 and C_3 - C_6) to (3349, 3313, 3379, 3359 and 3350) cm^{-1} respectively. This gives an indication that the ligand was coordinated with the metal ions through the nitrogen atom of α-amino group. The υ(N-H) stretching vibration band disappeared in the complex (C_2) because of the broad band related to mixing vibration of υ(N-H) stretching and lattice water. The band assigned to the stretching vibration of the υ(C≡N) group of (L_1) was shifted in the spectra of the complexes (C_1 and C_3-C_6) to lower frequencies (2169, 2154, 2173, 2208 and 2165) cm^{-1} respectively, which refers to the linkage of (C≡N) from nitrogen atom. The spectrum of complex (C_2) showed an increased shift in υ(C≡N) stretching vibration towards to higher frequencies as a result of coordination with metal ion through the lone pair electrons of nitrogen atom. The band assigned to the δ(N-H) bending vibration of the (NH) group of (L_1) was shifted in the spectra of the complexes (C_1- C_6) to (1653, 1653,1693,1658,1655 and 1655) cm^{-1} respectively, this gives further indication that the ligand which was coordinated with metal ions through the nitrogen atom of α-amino group and thus supports formation of complexes.

The band assigned to the υ(N-H) stretching vibration of the (NH) group of (L_2) ligand was shifted in the spectra of the complexes (C_{11} and C_{12}) to (3366 and 3356) cm^{-1} respectively. This gives an indication that the ligand was coordinated with the metal ions through the nitrogen atom of α-amino group, while in complexes (C_7- C_{10}) the υ(N-H) stretching vibration bands were disappeared because of the broad band related to mixing vibration of (N-H) stretching and lattice water. The band assigned to the stretching vibration of the (C≡N) group of (L_2) was shifted in the spectra of the complexes (C_7-C_{12}) towards to lower frequencies (2172, 2128, 2149, 2125, 2216 and 2220) cm^{-1} respectively, which indicates the linkage of (C≡N) group from nitrogen atom. The band assigned to the δ(N-H) bending vibration of the (NH) group of (L_2) ligand was shifted in the spectra of the complexes (C_7- C_{12}) towards to high frequencies (1654, 1699,1693,1699,1658 and 1658) cm^{-1} respectively, this gives further indication that the ligand was coordinated to the metal ions through the nitrogen atom of α-amino group.

Table 2- Characteristic infrared absorption bands of ligands (L_1 and L_2) and their complexes

Comp.	Molecular Formula	υN-H cm^{-1}	υC≡N cm^{-1}	υH_2O Lattice	δN-H cm^{-1}	υC-N cm^{-1}	υCH_3 cm^{-1}
L_1	**$C_{15}H_{14}N_2$**	**3329 V,S.Sh**	**2241 M,Sh**	--------	**1616 S,Sh**	**1125 S,Sh**	**1450 S,Sh**
C_1	**[Co $(L_1)_2Cl_2$].$2H_2O$**	**3349 S,Sh**	**2169 V,S.Sh**	**3141-3600**	**1653 S,Sh**	**1024 M,Sh**	**1450 S,Sh**
C_2	**[Cr $(L_1)_2Cl_2$]Cl.$3H_2O$**	--------	**2364 M,Br**	**3124-3562**	**1652 W,Br**	**1120 W,Br**	**1417 M,Sh**
C_3	**[Cu $(L_1)_2Cl(H_2O)$]Cl.H_2O**	**3313 W,Br**	**2154 M,Br**	**3130-3610**	**1693 W,Sh**	**1107 M,Sh**	**1448 M,Sh**
C_4	**[Ni $(L_1)_2Cl_2$].H_2O**	**3379 Br**	**2173 V.S,Sh**	**3100-3680**	**1658 V.S,Sh**	**1110 W,Sh**	**1456 S,Sh**
C_5	**[Zn $(L_1)_2Cl_2$].$2H_2O$**	**3359 V.S,Sh**	**2208 S,Sh**	**3137-3670**	**1655 S,Sh**	**1124 M,Sh**	**1450 S,Sh**
C_6	**[Fe $(L_1)_2Cl_2$]Cl.$2H_2O$**	**3349 V.S,Sh**	**2165 M,Sh**	**3120-3600**	**1654 S,Sh**	**1122 S,Sh**	**1450 S,Sh**
L_2	**$C_{14}H_{12}N_2$**	**3337 V.S,Sh**	**2250 M,Sh**	---------	**1601 V,S.Sh**	**1115 M,Sh**	--------
C_7	**[Co $(L_2)_2Cl_2$].$3H_2O$**	--------	**2172 V,S.Sh**	**3184-3525**	**1654 Sh,Sh**	**1101 Sh,Sh**	--------
C_8	**[Cr$(L_2)_2Cl_2$]Cl.$4H_2O$**	--------	**2128 M,Br**	**3159-3373**	**1699 W,Br**	**1122 M,Br**	--------
C_9	**[Cu$(L_2)_2Cl(H_2O)$]Cl.1.5H_2O**	--------	**2148 M,Sh**	**3220-3680**	**1693 M,Br**	**1094 M,Br**	--------
C_{10}	**[Ni $(L_2)_2Cl_2$].$2H_2O$**	--------	**2171 M,Sh**	**3151-3640**	**1699 W,Sh**	**1122 M,Sh**	--------
C_{11}	**[Zn $(L_2)_2Cl_2$].$3H_2O$**	**3366 S,Sh**	**2216 S,Sh**	**3128-3630**	**1658 S,Sh**	**1105 V,S.Sh**	--------
C_{12}	**[Fe$(L_2)_2Cl_2$]Cl.$3H_2O$**	**3356 V.S,Sh**	**2220 M,Sh**	**3120-3680**	**1658 V,S.Sh**	**1120 M,Sh**	--------

Where: S = Strong, M = Medium, W = Weak, V = Very, Br = Broad, Sh = Sharp

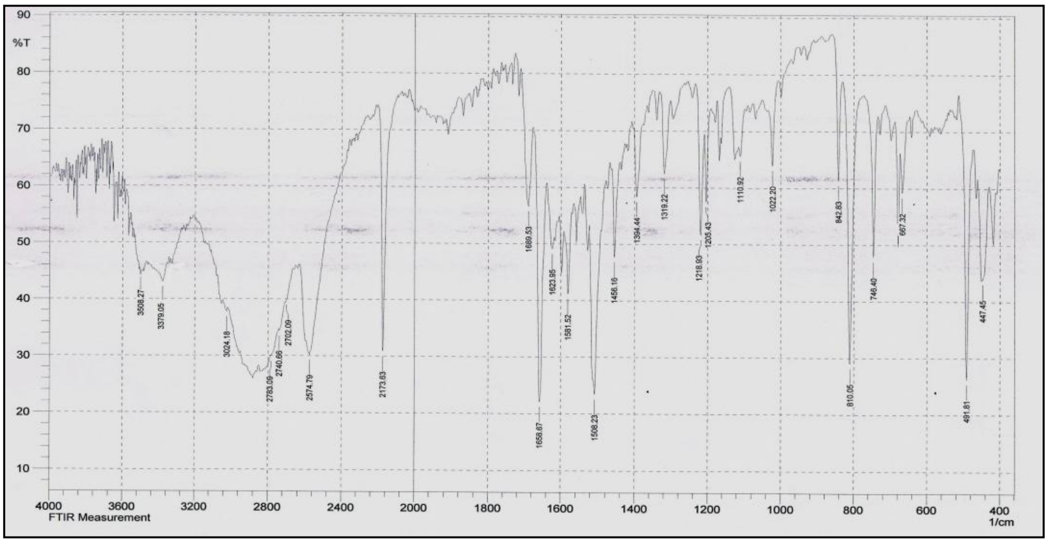


Figure 1-FTIR spectrum of C_4.

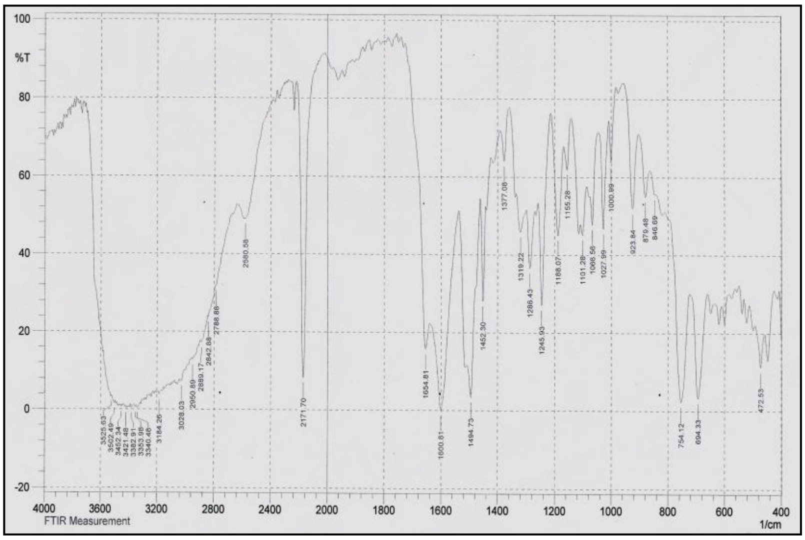


Figure 2-FTIR spectrum of C_7

^{1}H-NMR and ^{13}C-NMR Spectra

Both ligands (L_1 and L_2) were characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopic methods, in addition to eight complexes (C_1, C_2, C_4, C_5, C_7, C_9, C_{11}, and C_{12}) using DMSO as a solvent as shown in tables 3 and 4, figures 3 and 4. The ^{1}H-NMR spectra of the ligand (L_1) showed four peaks; The first one appeared at $\delta(2.33)$ ppm which corresponds to the ($-C\underline{H_3}$) protons, the second peak appeared at $\delta(3.57)$ ppm and was assigned to the ($-N-\underline{H}$) proton, while the third peak appeared at $\delta(5.34)$ ppm which was corresponded to the ($-C\underline{H}$ - $C\equiv N$). The last peak appeared at $\delta(6.57 - 7.67)$ ppm is attributed to the aromatic protons [18]. The spectra of the complexes (C_1, C_2, C_4 and C_5) were similar to that of the ligand, the only two difference was that the signal of (-N-H) of the ligand were shifted in these complexes by (0.12, 0.15, 0.17 and 0.16) ppm respectively, and the signal of ($-C\underline{H}$ - $C\equiv N$) were shifted in these complexes by (0.13, 0.12, 0.15 and 0.16) ppm respectively. This gave an indication for complexes formation. The ^{1}H-NMR spectra of the ligand (L_2) showed three peaks; the first one appeared at $\delta(4.05)$ ppm which corresponds to the ($-N-\underline{H}$) proton. The second peak appeared at $\delta(5.54)$ ppm and was attributed to the ($-C\underline{H}-C\equiv N$) proton and the last peak appeared at $\delta(6.55 - 7.47)$ ppm which corresponded to the aromatic protons [19]. The spectra of the complexes (C_7, C_9, C_{11} and C_{12}) were also similar to that of the ligand. The signal of ($N-\underline{H}$) of the ligands was shifted in these complexes by (0.60, 0.17, 0.16 and 0.22) ppm respectively and the signal of ($-CH-C\equiv N$) were shifted in these complexes by (0.14, 0.25, 0.18 and 0.42) ppm respectively, this gave an indication for complexes formation. The ^{13}C-NMR spectra of the ligand (L_1) showed three peaks; the first one appeared at $\delta(21.34)$ ppm which corresponded to the ($-\underline{CH_3}$) carbon, the second peak appeared at $\delta(55.14)$ ppm which corresponded to the ($-NH-\underline{C}H-C\equiv N$) carbon and the last peak appeared at $\delta(116.64)$ ppm which corresponded to the ($-CH-$ $\underline{C}\equiv N$) carbon [20]. The spectra of the complexes (C_1, C_2, C_4 and C_5) were similar to that of the ligand, the only difference was that the signal of ($-NH-\underline{C}H-C\equiv N$) carbon of the ligand was shifted in these complexes by (0.03, 0.05, 0.18 and 0.03) ppm respectively, and the signal of ($-CH-$ $\underline{C}\equiv N$) carbon were shifted in these complexes by (0.01, 0.01, 0.65 and 0.02) ppm respectively. The ^{13}C-NMR spectra of the ligand (L_2) showed two peaks; the first one appeared at $\delta(50.11)$ ppm which corresponded to the ($-\underline{C}H-$ $C\equiv N$) carbon, the second peak appeared at $\delta(113.64)$ ppm which corresponded to the ($-CH-$ $\underline{C}\equiv N$) carbon [20]. The spectra of the complexes (C_7, C_9, C_{11} and C_{12}) were similar to that of the ligand, the only difference was that the signal of ($-\underline{C}H-$ $C\equiv N$) carbon of the ligand was shifted in these complexes by (0.02, 0.01, 0.06 and 0.04) ppm respectively, and the signal of ($-CH-$ $\underline{C}\equiv N$) carbon were shifted in these complexes by (0.03, 0.05, 0.05 and 0.07) ppm respectively.

Table 3- ^{1}H-NMR data of ligands (L_1 and L_2) and some of their complexes

Comp	Molecular Formula	Groups	Chemical Shifts $\delta(ppm)$	Comp.	Molecular Formula	Groups	Chemical Shifts $\delta(ppm)$
L_1	$C_{15}H_{14}N_2$	-C$\underline{H_3}$ -N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	2.33 3.57 5.34 6.56-7.67	L_2	$C_{14}H_{12}N_2$	-NH -C$\underline{H}$- C≡N Ar-$\underline{H}$	4.05 5.54 6.55-7.47
C_1	$[Co(L_1)_2Cl_2].2H_2O$	-C$\underline{H_3}$ -N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	2.29 3.45 5.21 6.50-7.65	C_7	$[Co(L_2)_2Cl_2].3H_2O$	-N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	3.45 5.40 6.47-752
C_2	$[Cr(L_1)_2Cl_2]Cl.3H_2O$	-C$\underline{H_3}$ -N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	3.32 3.42 5.22 7.44-7.67	C_9	$[Cu(L_2)_2Cl(H_2O)]Cl.$ $1.5H_2O$	-N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	3.88 5.29 6.82-7.91
C_4	$[Ni(L_1)_2Cl_2].H_2O$	-C$\underline{H_3}$ -N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	2.28 3.40 5.19 6.87-7.49	C_{11}	$[Zn(L_2)_2Cl_2].3H_2O$	-NH -C$\underline{H}$- C≡N Ar-$\underline{H}$	3.89 5.36 6.52-7.69
C_5	$[Zn(L_1)_2Cl_2].2H_2O$	-C$\underline{H_3}$ -N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	2.34 3.41 5.18 6.84-7.67	C_{12}	$[Fe(L_2)_2Cl_2]Cl.3H_2O$	-C-N$\underline{H}$ -C$\underline{H}$- C≡N Ar-$\underline{H}$	3.83 5.12 6.78-7.83

Table 4- ^{13}C-NMR data of ligands (L_1 and L_2) and some of their complexes

Comp	Molecular Formula	Groups	Chemical Shifts $\delta(ppm)$	Comp.	Molecular Formula	Groups	Chemical Shifts $\delta(ppm)$
L_1	$C_{15}H_{14}N_2$	-$\underline{C}H_3$ -NH-$\underline{C}$H- C≡N -CH- $\underline{C}$≡N	21.34 55.14 116.64	L_2	$C_{14}H_{12}N_2$	-$\underline{C}$H- C≡N CH- $\underline{C}$≡N	50.11 113.64
C_1	$[Co(L_1)_2Cl_2].2H_2O$	-$\underline{C}H_3$ -NH-$\underline{C}$H- C≡N -CH- $\underline{C}$≡N	21.345 55.11 116.63	C_7	$[Co(L_2)_2Cl_2].3H_2O$	-$\underline{C}$H- C≡N CH- $\underline{C}$≡N	50.09 113.61
C_2	$[Cr(L_1)_2Cl_2]Cl.3H_2O$	-$\underline{C}H_3$ -NH-$\underline{C}$H- C≡N -CH- $\underline{C}$≡N	20.61 55.09 116.63	C_9	$[Cu(L_2)_2Cl(H_2O)]Cl.$ $1.5H_2O$	-$\underline{C}$H- C≡N CH- $\underline{C}$≡N	50.10 113.59
C_4	$[Ni(L_1)_2Cl_2]. H_2O$	-$\underline{C}H_3$ -NH-$\underline{C}$H- C≡N -CH- $\underline{C}$≡N	20.27 54.96 115.99	C_{11}	$[Zn(L_2)_2Cl_2].3H_2O$	-$\underline{C}$H- C≡N CH- $\underline{C}$≡N	50.05 113.59
C_5	$[Zn(L_1)_2Cl_2].2H_2O$	-$\underline{C}H_3$ -NH-$\underline{C}$H- C≡N -CH- $\underline{C}$≡N	21.33 55.11 116.62	C1$_2$	$[Fe(L2)_2\ Cl_2]Cl.3H_2O$	-$\underline{C}$H- C≡N CH- $\underline{C}$≡N	50.07 113.57

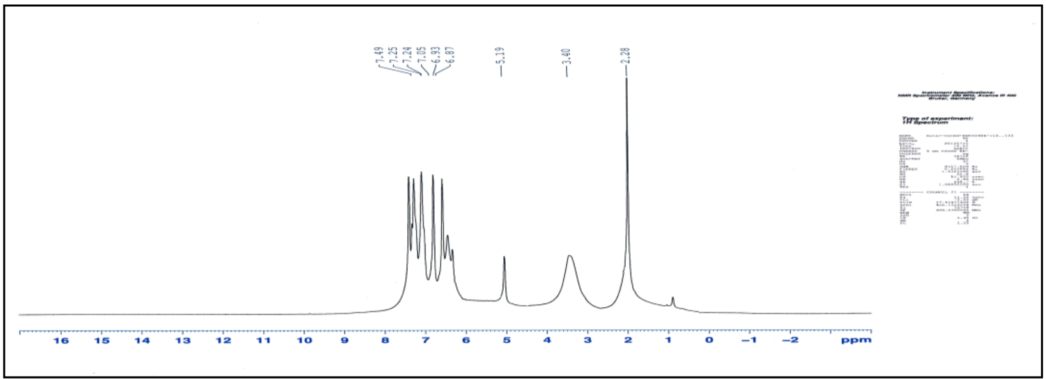


Figure 3-^{1}H-NMR spectra of the complex C_4

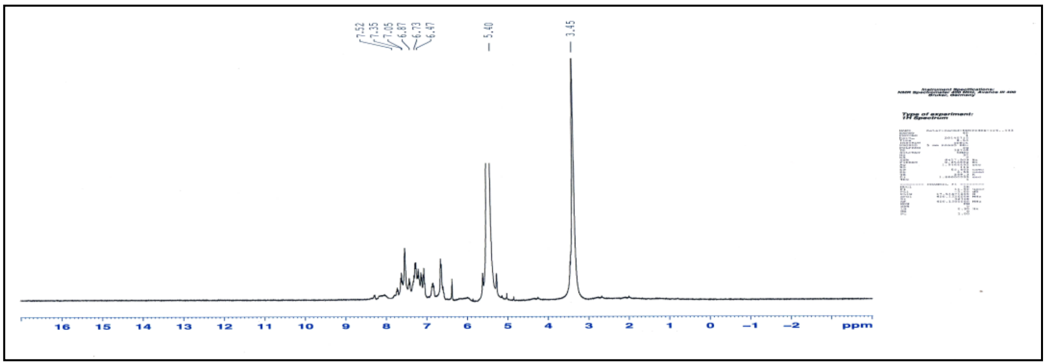


Figure 4-^{1}H-NMR spectra of the complex C_7

Molar Conductance:

The molar conductance of all the prepared complexes (10^{-3}M) was measured in ethanol at room temperature. The values of the molar conductance of the complexes (C_1, C_4, C_5, C_7, C_{10}, and C_{11}) lied in the range of (14-22) Ω^{-1}.cm^2.mol^{-1}, these values indicated that these complexes were non electrolytes, this mean that all the chloride anions are coordinated to the metal ion inside the coordination sphere, while molar conductance values of complexes (C_2, C_3, C_6, C_8, C_9 and C_{12}) lied in the range of (29-42) Ω^{-1}.cm^2.mol^{-1}, these values indicated that these complexes were weak electrolytes, and that for complexes (C_2, C_6, C_8 and C_{12}) there were two chloride anions coordinated to the metal ion, leaving the other chloride anion outside the coordination sphere, while the complexes (C_3 and C_9) there were only one chloride anion coordinate to the metal ion, leaving the other chloride anion outside the coordination sphere [21]. The values of molar conductance of the complexes are shown in table 5.

Table 5- Electronic spectra, spectra parameters, molar conductance, magnetic susceptibility and suggested stereo chemical of ligands and their complexes

Comp.	**Molecular formula**	λ **nm**	$\bar{\upsilon}$ **cm^{-1}**	**Assignment**	**Molar conductance (Ω^{-1}cm^{2}mol^{-1})**	**Magnetic susceptibility µ *eff* (B.M)**	**Suggested Geometry**
L_1	$C_{15}H_{14}N_2$	290 242	34482 41322	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--------	--------	--------
C_1	$[Co(L_1)_2Cl_2].2H_2O$	936 764 634	10685 12880 15766	$^4T_1g(F) \rightarrow {}^4T_2g(F)$ $^4T_1g(F) \rightarrow {}^4A_2g$ $^4T_1g(F) \rightarrow {}^4T_1g(P)$	18.4	4.03	Octahedral
C_2	$[Cr(L_1)_2Cl_2]Cl.3H_2O$	757 566 364	13210 17654 27490	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g(F)$ $^4A_2g \rightarrow {}^4T_1g(P)$	35.2	3.78	Octahedral
C_3	$[Cu\ (L_1)_2Cl(H_2O)]Cl.\ H_2O$	698	14326	$^2Eg \rightarrow {}^2T_2g$	36.5	1.89	Distorted Octahedral
C_4	$[Ni(L_1)_2Cl_2].\ H_2O$	602 425	16611 23529	$^3A_2g \rightarrow {}^3T_1g$ $^3A_2g \rightarrow {}^3T_1g(p)$	17.8	2.81	Octahedral
C_5	$[Zn(L_1)_2Cl_2].2H_2O$	486	20576	$L \rightarrow M$ (CT)	14.1	Diamagnetic	Octahedral
C_6	$[Fe\ (L_1)_2Cl_2]Cl.2H_2O$	531 467	18832 21413	$^6A_1g \rightarrow {}^4T_2g\ (G)$ $^6A_1g \rightarrow {}^4A_1g + {}^4Eg$	31.7	5.19	Octahedral
L_2	$C_{14}H_{12}N_2$	283 240	35335 41666	$n \rightarrow \pi^*$ $\pi \rightarrow \pi^*$	--------	--------	--------
C_7	$[Co(L_2)_2Cl_2].3H_2O$	787 674 575	12706 14836 17391	$^4T_1g(F) \rightarrow {}^4T_2g(F)$ $^4T_1g(F) \rightarrow {}^4A_2g$ $^4T_1g(F) \rightarrow {}^4T_1g(P)$	21.6	4.18	Octahedral
C_8	$[Cr(L_2)_2Cl_2]Cl.4H_2O$	743 542 362	13460 18456 27660	$^4A_2g \rightarrow {}^4T_2g$ $^4A_2g \rightarrow {}^4T_1g(F)$ $^4A_2g \rightarrow {}^4T_1g(P)$	34.3	3.99	Octahedral
C_9	$[Cu(L_2)_2Cl(H_2O)]Cl.1.5H_2O$	740	13513	$^2Eg \rightarrow {}^2T_2g$	42.8	1.79	Distorted Octahedral
C_{10}	$[Ni\ (L_2)_2Cl_2].2H_2O$	525 440	19047 22727	$^3A_2g \rightarrow {}^3T_1g$ $^3A_2g \rightarrow {}^3T_1g(p)$	22.5	3.1	Octahedral
C_{11}	$[Zn(L_2)_2Cl_2].3H_2O$	496	20161	$L \rightarrow M$ (CT)	18.2	Diamagnetic	Octahedral
C_{12}	$[Fe(L_2)_2\ Cl_2]Cl.3H_2O$	526 458	19011 21834	$^6A_1g \rightarrow {}^4T2g\ (G)$ $^6A_1g \rightarrow {}^4A_1g+{}^4Eg$	29.5	5.62	Octahedral

U.V-Visible:

The electronic absorption data of the ligands (L_1 and L_2) and their complexes in ethanol at room temperature are shown in table 5 and the UV spectra of some complexes were illustrated in figures 5 and 6. The spectra of two lignds exhibited a high intensity band appeared in the region at (41322, 41666) cm^{-1} respectively assigned to $\pi - \pi^*$ of conjugated system [22]. Low intensity bands appeared in the near U.V. region (34482, 35335) cm^{-1} respectively were assigned to $n - \pi^*$ transition, the intensity and positions of these bands depends on the structure of molecules and nature of the solvent used [23]. The electronic spectra of complexes exhibited the appearance of new bands, the intensities and positions of these bands are mainly dependent on electron configuration of metal ions, stereochemistry of complexes and ligand field effects [24].

i- Cobalt (II) Complexes (C_1 and C_7):

The spectra of the complexes (C_1 and C_7) showed three bands observed at (10685, 12880 and 15766) cm^{-1} and (12706, 14836 and 17391) cm^{-1} respectively, these bands may be assigned to the transitions $^4T_1g(F) \rightarrow {}^4T_2g(F)$, $^4T_1g(F) \rightarrow {}^4A_2g$ and $^4T_1g(F) \rightarrow {}^4T_1g(P)$ respectively. The magnetic moment values (4.03, 4.18) B.M was in accordance with those having octahedral structure [25].

ii- Chrome (III) Complexes (C_2 and C_8):

The spectra of the complexes (C_2 and C_8) showed three bands observed at (13210, 17654, and 27490) cm^{-1} and (13460, 18456 and 27660) cm^{-1} respectively, these bands may be assigned to the transitions $^4A_2g \rightarrow {}^4T_2g$, $^4A_2g \rightarrow {}^4T_1g(F)$ and $^4A_2g \rightarrow {}^4T_1g(P)$ respectively. The magnetic moment values (3.70, 3.88) B.M was in accordance with those having octahedral structure [26].

iii- Copper (II) Complexes (C_3 and C_9):

The spectra of the complexes (C_3 and C_9) showed one band observed at (14326 and 13513) cm^{-1} respectively these bands may be assigned to the transitions $^2Eg \rightarrow {}^2T_2g$. The magnetic moment values (1.89, 1.72) B.M was in accordance with those having distorted octahedral structure [27].

iV- Nickel (II) Complexes (C_4 and C_{10}):

The spectra of the complexes (C4 and C10) showed two bands observed at (16611 and 23529) cm^{-1} and (19047 and 22727) cm^{-1}, respectively these bands may be assigned to the transitions $^3A_2g \rightarrow {}^3T_1g$ and $^3A_2g \rightarrow {}^{3T1g}$ (p). The magnetic moment values (2.85, 3.1) B.M was in accordance with those having octahedral structure [28].

V- Zinc (II) Complexes (C_5 and C_{11}):

The spectra of the complexes (C_5 and C_{11}) showed one peak at (20576 and 20161) cm^{-1} due to charge transfer from ligand to metal. The magnetic moment value for these complexes was zero, indicating diamagnetic nature of the complex and octahedral geometry [27].

Vi. Iron (III) Complexes (C_6 and C_{12}):

The spectra of the complexes (C_6 and C_{12}) showed two bands observed at (18832 and 21413) and (19011 and 21834), respectively, these bands may be assigned to the transitions $^6A_1g \rightarrow {}^4T_2g$ (G) and $^6A_1g \rightarrow {}^4A_1g + {}^4Eg$. The magnetic moment values (5.19, 5.62) B.M was in accordance with those having high spin Fe(III) octahedral complexes [29].

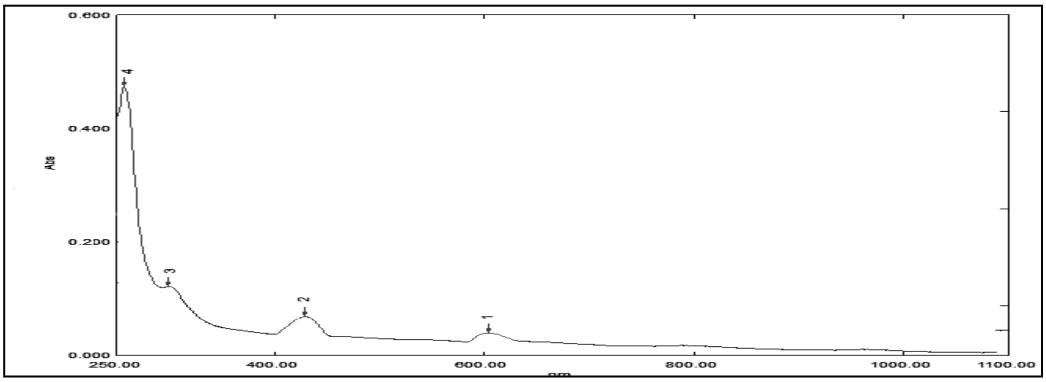


Figure 5-U.V spectrum of C_4

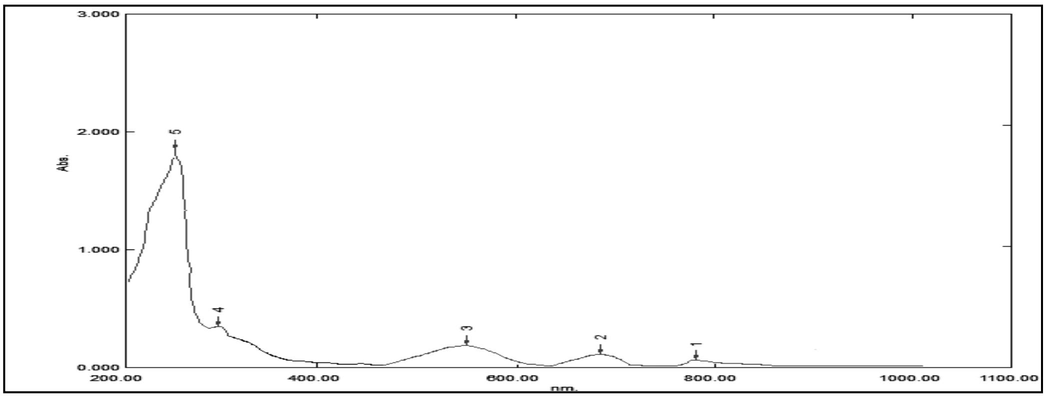


Figure 6-U.V spectrum of C_7

Thermal analysis of complexes:

Thermal decomposition of complexes (C_1-C_{12}) follows TGA techniques and heating range (30-450)°C. The thermal decomposition data for all complexes are given in table 6, figures 7 and 8.

1. The first stage which took place at temperature range of (50-150)°C. It is hard at this point to differentiate between the coordinated water and uncoordinated (Lattice water) from the thermographs [30, 31].
2. The following stages include the departure of chloride at temperatures depending on bond energies resulted from coordination of ligand atoms [32].
3. The final stage of thermal decomposition of complexes gave metal oxide or free metal as final reside depending on the type of metal ion and on (M-L) affinity [33].

Table 6- Thermal decomposition data for complexes

Comp	Molecular formula	Step	Temp. rang of the decomposition C°	Suggested formula of resultant compound	Mass loss %	
					Cal	Found
C_1	$[Co(L_1)_2Cl_2].2H_2O$	1	70-112	$[Co(L_1)_2Cl_2]$	5.9	5.5
		2	112-180	$[Co(L_1)_2]$	11.6	11.1
		3	180-375	CoO	72.7	71.9
C_2	$[Cr(L_1)_2Cl_2]Cl.3H_2O$	1	65-140	$[Cr(L_1)_2Cl_2]Cl$	8.2	8.0
		2	140-190	$[Cr(L_1)_2]$	16.2	16.0
		3	190-365	Cr_2O_3	67.4	67.0
C_3	$[Cu (L_1)_2Cl(H_2O)]Cl. H_2O$	1	65-130	$[Cu (L_1)_2Cl]Cl$	5.8	5.4
		2	130-170	$[Cu(L_1)_2]$	11.5	11.2
		3	170-390	CuO	72.2	71.5
C_4	$[Ni(L_1)_2Cl_2]. H_2O$	1	55-100	$[Ni(L_1)_2Cl_2]$	3.0	2.7
		2	100-160	$[Ni(L_1)_2]$	11.9	11.5
		3	160-380	NiO	75.0	74.2
C_5	$[Zn(L_1)_2Cl_2].2H_2O$	1	50-105	$[Zn(L_1)_2Cl_2]$	5.8	5.4
		2	105-175	$[Zn(L_1)_2]$	11.5	11.0
		3	175-380	ZnO	72.0	71.2
C_6	$[Fe (L_1)_2Cl_2]Cl.2H_2O$	1	50-115	$[Fe (L_1)_2Cl_2]Cl$	5.6	5.0
		2	115-200	$[Fe (L_1)_2]$	16.5	16.0
		3	200-385	Fe_2O_3	69.1	68.5
C_7	$[Co(L_2)_2Cl_2].3H_2O$	1	60-130	$[Co(L_2)_2Cl_2]$	9.0	8.5
		2	130-190	$[Co(L_2)_2]$	11.8	11.2
		3	190-370	CoO	69.3	68.5
C_8	$[Cr(L_2)_2Cl_2]Cl.4H_2O$	1	60-140	$[Cr(L_2)_2Cl_2]Cl$	11.1	10.6
		2	10-195	$[Cr(L_2)_2]$	16.4	16.0
		3	195-360	Cr_2O_3	64.3	63.6
C_9	$[Cu(L_2)_2Cl]Cl(H2O)]1.5H_2O$	1	50-150	$[Cu(L_2)_2Cl]Cl$	7.5	7.0
		2	150-190	$[Cu(L_2)_2]$	11.9	11.5
		3	190-380	CuO	69.8	69.0
C_{10}	$[Ni (L_2)_2Cl_2].2H_2O$	1	55-120	$[Ni (L2)_2Cl_2]$	6.1	5.7
		2	120-170	$[Ni (L_2)_2]$	12.2	11.9
		3	170-375	NiO	71.5	70.8
C_{11}	$[Zn(L_2)_2Cl_2].3H_2O$	1	50-105	$[Zn(L_2)_2Cl_2]$	8.9	8.5
		2	105-155	$[Zn(L_2)_2]$	11.7	11.2
		3	155-375	ZnO	68.6	68.1
C_{12}	$[Fe(L_2)_2 Cl_2]Cl.3H_2O$	1	55-130	$[Fe(L_2)_2 Cl_2]Cl$	8.5	8.2
		2	130-215	$[Fe(L_2)_2]$	16.8	16.1
		3	215-380	Fe_2O_3	65.7	65.2

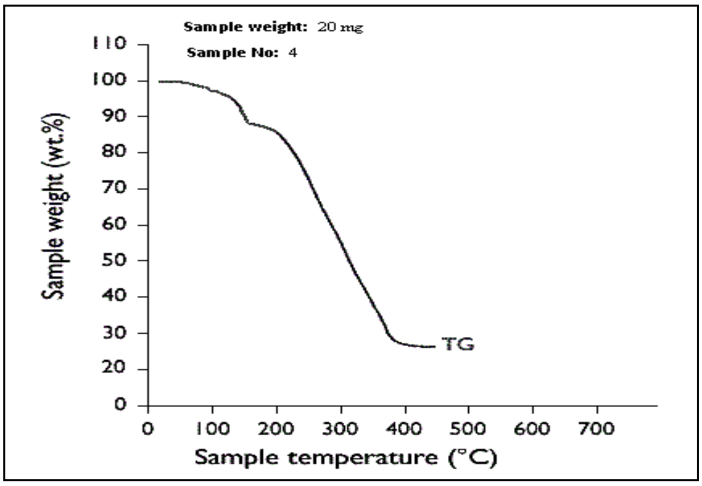


Figure 7-Thermograph of C_4

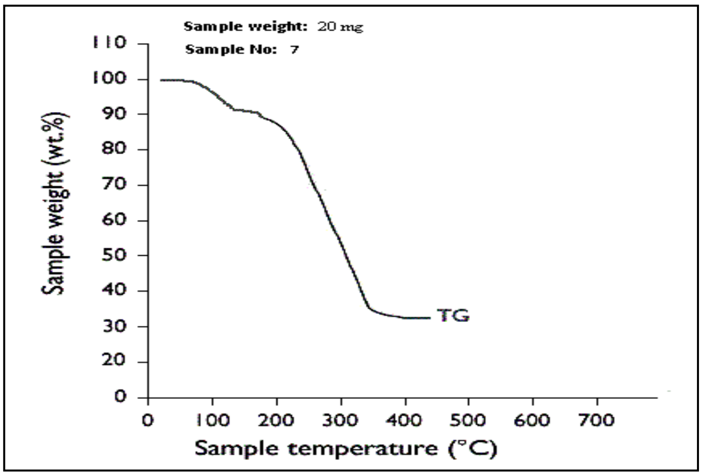
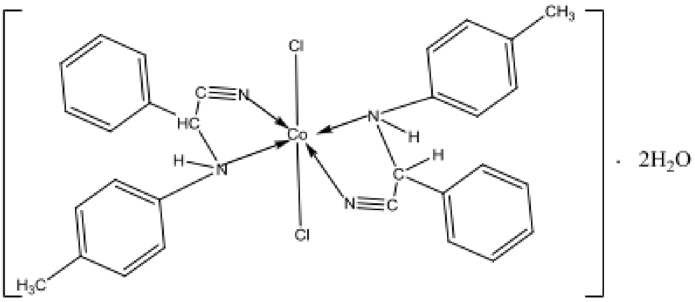


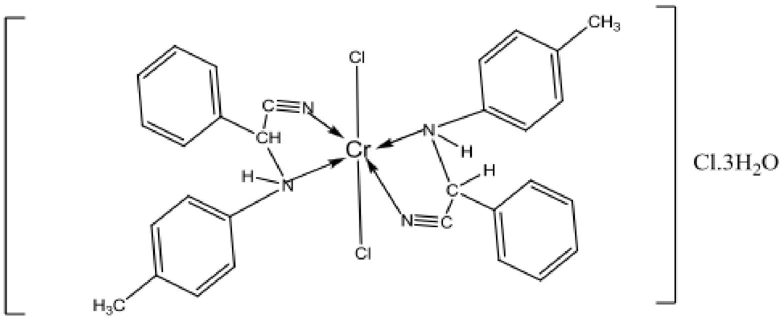
Figure 8-Thermograph of C_7

According to the above-mentioned data the structures of twelve metal complexes can be suggested as instated in scheme 2.



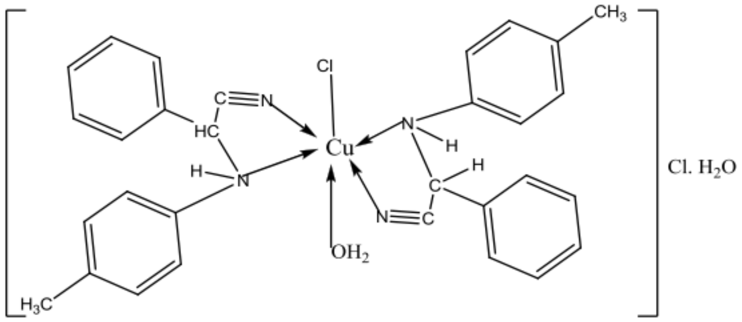
$[Co(L_1)_2Cl_2].2H_2O$

C_1: [Di Chloro-bis{2-phenyl-2-(*p*-tolylamino) acetonitrile} Cobalt (II)](2)Hydrate



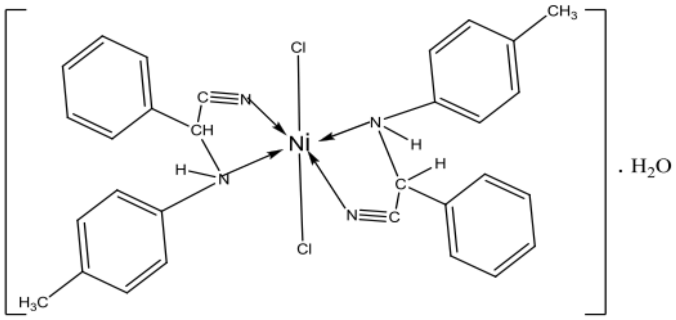
$[Cr(L_1)_2Cl_2]Cl.3H_2O$

C_2: [Di Chloro-bis{2-phenyl-2-(*p*-tolylamino)acetonitrile}Chrome(III)] Chloride (3) Hydrate



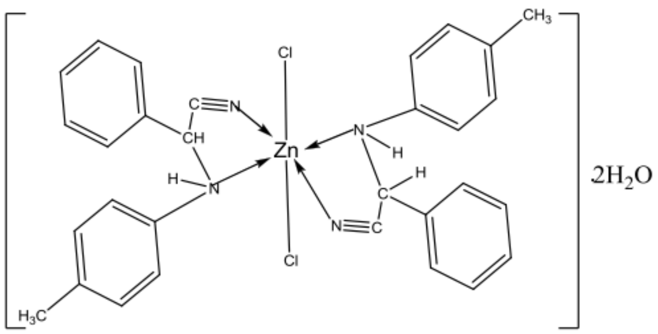
$[Cu(L_1)_2Cl(H_2O)]Cl.H_2O$

C_3: [Chloro monoaqua-bis {2-phenyl-2-(*p*-tolylamino) acetonitrile} Copper (II)]Chloride] (1) Hydrate



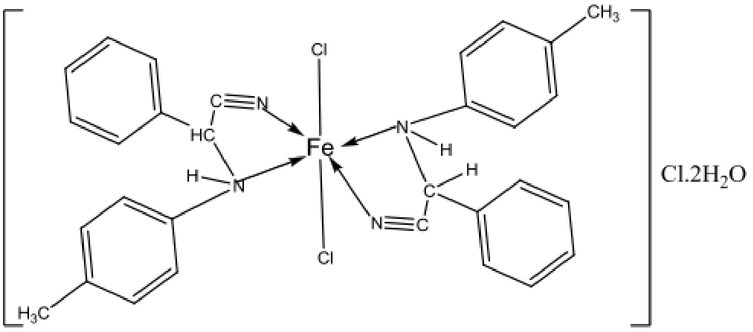
$[Ni (L_1)_2Cl_2].H_2O$

C_4: [Di Chloro-bis {2-phenyl-2-(*p*-tolylamino) acetonitrile} Nickel (II)](1)Hydrate



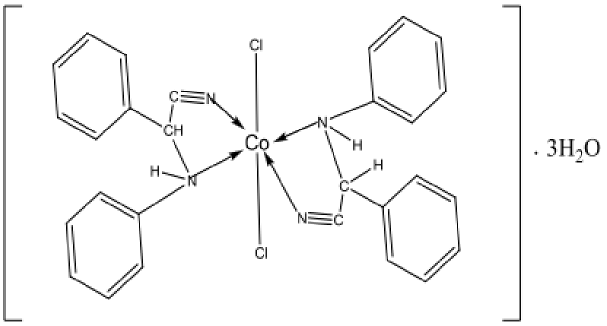
$[Zn (L_1)_2Cl_2].2H_2O$

C_5: [Di Chloro-bis {2-phenyl-2-(*p*-tolylamino) acetonitrile} Zinc(II)](2)Hydrate



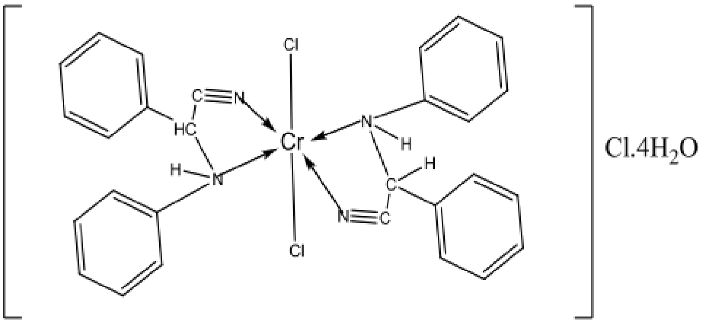
[Fe $(L_1)_2Cl_2]Cl.2H_2O$

C_6: [Di Chloro-bis{2-phenyl-2-(*p*-tolylamino)acetonitrile}Iron(III)] Chloride (2) Hydrate



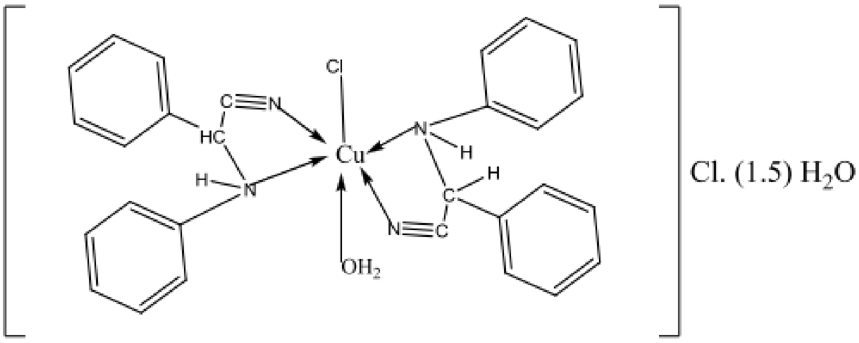
[Co $(L_2)_2Cl_2].3H_2O$

C_7: [Di Chloro-bis {2-phenyl-2-(phenylamino)acetonitrile }Cobalt (II)](3)Hydrate



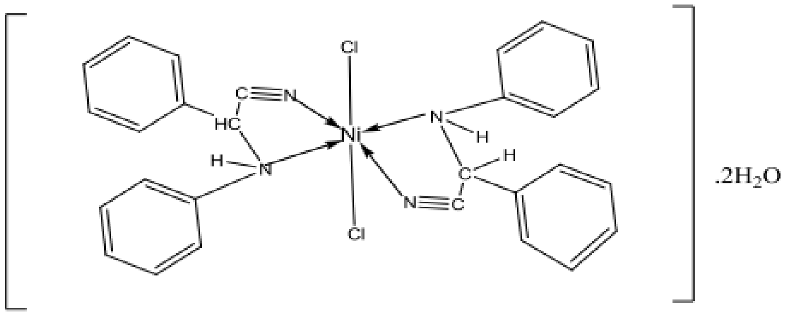
[Cr $(L_2)_2Cl_2]Cl.4H_2O$

C_8:[Di Chloro-bis{2-phenyl-2-(phenylamino)acetonitrile }Chrome(III)] Chloride (4) Hydrate



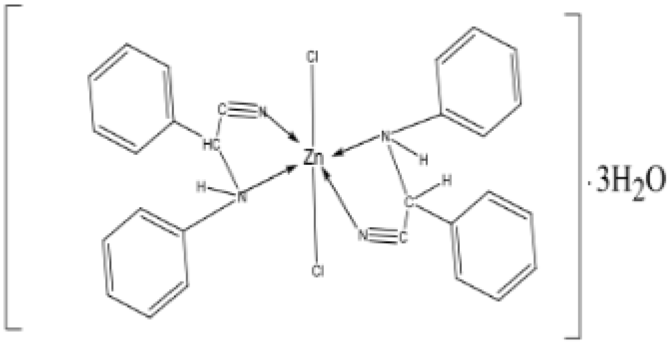
[Cu $(L_2)_2Cl(H_2O)]Cl.(1.5)H_2O$

C_9:[Chloro mono aqua-bis {2-phenyl-2-(phenylamino)acetonitrile }Copper(II)]Chloride (1.5) Hydrate



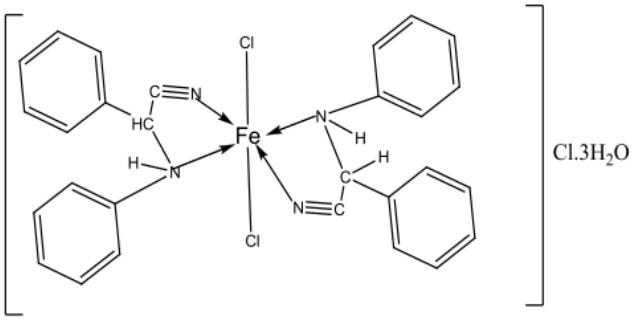
[Ni (L$_2$)$_2$Cl$_2$].2H$_2$O

C$_{10}$: [Di Chloro-bis {2-phenyl-2-(phenylamino)acetonitrile } Nickel(II)](2)Hydrate



[Zn (L$_2$)$_2$Cl$_2$].3H$_2$O

C$_{11}$: [Di Chloro-bis {2-phenyl-2-(phenylamino)acetonitrile } Zinc (II)](3)Hydrate



[Fe (L2)$_2$Cl$_2$]Cl.3H$_2$O

C$_{12}$: [Di Chloro-bis{2-phenyl-2-(phenylamino)acetonitrile }Iron(ııı)] Chloride (3) Hydrate

Conclusions:

In this study, the prepared compounds represent a group of bidentate ligands exhibiting good chelating properties. The presence of two donor atoms in these ligands may give various polynuclear metal complexes. In all complexes, the coordination of ligands to the metal ions took place through the nitrogen atom of cyanide and amine groups. All complexes showed octahedral geometry around metal ions.

References

1. Strecker. Ann.**1850.**The artificial formation of lactic acid and a new glycerol homologous body.*Chem. Pharm*, .75, pp: 27-45.
2. March, J. **1985**. *Advanced organic chemistry*. 3rd Ed, Wiley-Interscience, New Jersey pp: 855-856.
3. Mai. K. Patel, G. **1985**. A fast n-substituted α-Aminonitrile synthesis, *Syn.Comm*, .15, pp: 157-163.
4. Kalir. A. Edery, H. Pelah.Z.D and Porath. G.**1969.** I-Phenylcoalkylamine derivatives, synthesis and pharmacological activity, *J.Med. Chem*, .12, pp 473-477.

5. Suresh and Jagir S. Sandhu. **2009**. Alum Catalyzed Efficient one pot synthesis of α-aminonitriles .*Rasayan J.Chem*, .2(1), pp: 182-185.

6. Van.Nhien, A. N. Pillon, M. Villa. P and Ronco. G. **2000**. Steroselective synthesis of aminonitriles at non- anomeric position of monosaccharides, *Tetrahedron* Letters, .41, pp: 6403-6406.

7. Foust. R. D, J. R and Ford.P. C. **1972**. The preparation and properties of some organonitrile complexes of pentamminerhodium (III), *Inorganic Chemistry*, .11 :(4): pp 899-901.

8. Undavia. N. K., Patwa. B.S., Navadiya. H. D. and Jivani. A. R. **2009**. Synthesis and biological evalution of some new α-aminonitrile derivatives, *Int. J. Chem*, 7(2), pp: 672-680.

9. Kumar, G. and Kiremire, E.M.R. **2007**. Synthesis, coordination and structure of mixed ligand copper (II) complexes of iminodiacetic acid and hippuric acid. *Chemistry*.16 (5), pp: 386-92.

10. Subodh.Kumar.**2006**. *Spectroscopy of organic compounds*. Guru.Nanak University. Amritsar. India. pp25.

11. Bernstein. M. P. Bauschlicher. C. W. Jr. and Sandford. S. A. **2004**. The infrared spectrum of matrix isolated amino acetonitrile, a precursor to the amino acid glycine, *Advances in Space Research*, 33, pp: 40-43.

12. Cooper.J. W. **1980**. *Spectroscopic techniques for organic chemists*. John Wiley & Sons, New York, pp 304.

13. Silverstein, Bassler and Morrill. **1981**. *Spectrrometric identification of organic compounds* 4th Edition, John Wiley & Sons, New York, pp 304.

14. Frank. S. Parker. **1971**. *Infrared spectroscopy, biology and medicine*. Plenum Press, New York, pp102.

15. David. Dolphen. **1977**. *Tabulation of infrared spectral data*, John Wiley & Sons, New York, pp: 123.

16. Stuart. B. **2004**. *Infrared spectroscopy, fundamental and application*, John Wiley & Sons, New York, pp 80.

17. Max. P. Bernstein, Charles. W. Baushlicher.Jr and Scoot.A. **2003**. Sandford, The infrared spectrum of matrix isolated aminoacetonitrile, *Advances in Spase Research* , 33, pp :40-43.

18. Surya. G. K. Prakash, Tisa. Elizabeth. Thomas, Inessa. Bychinskaya and Arjun. Prakash. **2008**. Efficient green synthesis ofα-aminonitriles , precursors of α-amino acids, *Royal Society of Chemistry*, .10, pp 1105-1110.

19. Raghu M. and Sanjeeva.Ch. Raddy. **2008**. $ZrCl_4$ promoted efficient one pot synthesis of α-aminonitriles , *Indian Journal of Chemistry*, .48:(B), pp 295-300.

20. Alejandro. Baeza, Carmen. Najera and Jose. M. Sansano. **2008**. Solvent free synthesis of racemic α-aminonitriles,Template for synlett and synthesis, *Thieme Stuttgart*, pp1-7.

21. Geary.W. J. **1971**. The use of conductivity measurements in organic solvents for the characterization of coordination compounds, *Coordination chemistry*. *Rev* , .7, pp 81-122.

22. Foust. R. D, J. R and Ford. P. C. **1972**. The preparation and properties of some organonitrile complexes of pentammine rhodium (III), *Inorganic Chemistry,* .11(4): pp 899-901.

23. Nada. M. Abbas. **2006**. Synthesis and characterization and study of the biological activity of new mannich-Shiff bases and some metal complexes derived from istatin, 3- amino-1,2.4-triazole and dithiooxamide ,ph.D, thesis, University of Baghdad, College of Science.

24. Melson. G. A. **1979**. *Coordination chemistry of micro cyclic compounds*, Plenum press, New York, pp 345-392.

25. Sahbaa. A. Al-Sabaawi. **2011**. Synthesis and Characterization of some Mononuclear Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) Complexes containing Bis-(2- thiophenelidene) thiosemicarbazone ligand. *Education Researchers Journal*, .11:3, pp765-776.

26. Dubey. R. K, Dubey. U. K and Mishra. C. M. **2008.** Synthesis and physicochemical characterization of some shiff base complexes of chromium(III). *Indian Journal of Chemistry*, .47: (A), pp 1208-1212.

27. Pragathi. B. Anupama and C. Gyanakumari. **2012**; Synthesis, spectral Characterization,Molecular Modeling, and Antimicrobial Studies of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) Complexes of ONO Schiff Base. *E-Journal of Chemistry*, .4:(9), pp 2145-2154.

28. 28. Lever. A. B. **1968**.The electronic spectra of tetragonal metal complexes analysis and significance, *Coordination Chemistry Reviews*, . 3:(2), pp 119-140.

29. Alshareefi. A. N., S. H. K and W. A. J. **2013**. Synthesis and study of Fe(III), Co(II),Ni(II) and Cu(II) complexes of new Schiff base ligand derived from 4-amino antipyrine, *Journal of Applicable Chemistry*, .2:(3), pp 438-446.

30. Yin. C. M., Kong Y. H., Liu. Z. R., Wu. C. Y., Ren. D. H., He. M. A. and Xue. H. F. .**1989**; Studies on the thermal behavior and decomposition mechanism of complexes of rare earth (III) nitrates, *Journal of Analysis*,. 35, pp2471-2479.

31. Tongbu. L., Xinmin. G., Ning. T. and Minyu. T. **1990**. Studies on rare earth complexes with crown ethers, synthesis and characterization of the complexes of lanthanide thiocyanates with dibenzo-24-crown-8, *Polyhedron*, .9 :(19), pp2371-2374.

32. Das. P. K., Nayak. S. C. and Khatua. S. K., **2014**.Synthesis and characterization of some iron(III) complexes containing heterocyclic nitrogen donor ligands, *Ind. J. Sci. Res and Tech*, .2:(1), pp9-15.

33. Allan. J. R. and Rentos. A. **1990**. Thermal studies on pyridine-3,4-dicarboxylic acid compound of cobalt, nickel and copper, *Thermochimica Acta*,.161, pp111-118.