Synthesis and Characterisation of Schiff Base Macrocycle Ligand Contain the Nitrogen and Oxygen as Donor Atoms and Their Complexes with Some Metal Ions

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Abstract:

The macrocyclic type ligand contain the nitrogen and oxygen as donor atoms have been prepared *via* the template reaction in two steps with their complexes of some metal ions, the reaction of one equivalent 2,5-hexanedione and two equivalent of *O*-hydroxyaniline obtained the precursor which the used in the template reaction since the 1,3-dibromopropane and metal salts were added together as 1:1 ratio to the solution of precursor to form the complexes. The prepared compounds were characterised by FT-IR, UV-Vis, HNMR spectroscopies, solubility, conductivity, and magnetic susceptibility. The spectral and physical studies show the suggested geometry around the metals is distorted octahedral.

الخلاصة:-

حضر ليكند حلقة كبيرة حاوية على النيتروجين والاوكسجين كذرات مانحة من خلال تفاعل القالب ، حيث حضر الليكند ومعقداته بخطوتين تضمنت الخطوة الاولى تحضير المشتق من خلال تفاعل مكافئ واحد من 2،5-هكسان ثنائي كيتون مع مكافئين من اورثوهايدروكسي انلين. تم استخدام المشتق المحضر وبطريقة القالب لانتاج الليكند ومعقداته من خلال اضافة مكافئ واحد من كل من 1،3-ثنائي برومو بروبان وملح الفلز لينتج معقد الفلز المعني. شخصت المركبات المعنية بواسطة مطيافية الاشعة تحت الحمراء وفوق البنفسجية المرئية وطيف الرنين النووي المغناطيسي اضافة الى دراسة الذوبانية والتوصيلية والحساسية المغناطيسية. واوضحت الدراسات الطيفية والقياسات الفيزياوية ان الشكل المقترح لهذه المعقدات هو ثماني السطوح المشوه.

INTRODUCTION

The Schiff base macrocycle ligands and their complexes play an essential role in the various fields such as agriculture, pharmaceutical, and industrial chemistry (1-3). More than one of complexes found act as *antimicrobial* agent such as complexes of Mo(IV) and Mn(II) with ligands hydrazine carboxamide and hydrazine carbothiamide show *antibacterial* activity against S. aureus and Xanthomonas compestrise(4-6). The divalent ions of zinc, cadmium nickel and copper complexes with semicarbazide and furfural Schiff base show *antibacterial* activities (7-11). The miscellaneous application of Schiff base ligands to bind of the proteins within nuclear membrane with Cu(II) and Zn(II) complexes, the organocobalt complexes with tridentate Schiff base act as initiator of emulsion polymerisation and copolymerisation of dienyl and vinyl monomers(12-15). Recent studies on macrocyclic complexes containing mixed nitrogen, sulfur, and/or oxygen donor atoms(16), show that it remains an active area of research. Elegant studies on ligand design and metal ion recognition of macrocyclic complexes have been reported by Lindoy(17-19) and co-workers. Evidently, transition metals can act as templates(20) for the synthesis of many macrocyclic complexes. A wide variety of macrocyclic complexes were reported by Martell(21-22) where he added a note on the catalytic activity of Cu complexes(22).

$[ML^1Cl_2]$ $[ML^2Cl_2]$

M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+}

Scheme 1

Experimental part

All reagents were commercially available (Aldrich Chemical Company) and were used without further purification. The solvent used in the synthesis were distilled from the appropriate drying agent immediately prior to use all manipulations in the synthesis of precursor and template ligand complexes were performed under Nitrogen atmosphere.

Electronic spectra were measured in the region 200-800 nm for solution methanol at room temperature using a Perkin Elmer precisely UV-Vis spectrophotometer. Infrared spectra were recorded by using a Shimadzu – 300 FTIR spectrometer. HNMR spectra were recorded in DMSO-d6 using a JEOL – JNM-ESC400.

Synthesis of precursor

In the round bottomed flask three neck 250 mL in size putted (5.73g, 0.052 mmol.) from 2-hydroxyaniline dissolved in 15 mL of ethanol with stirring for 10 minutes to completely miscible, the added (3.08g, 0.02 mmol.) from 2,5-hexanedione mixed with 5 mL of ethanol. The mixture was let to stirring 10 minutes and refluxed for two hours at temperature range between (65-75) ^{0}C. Observed the colour of solution became purple, let to cool at room temperature and recrystallised with methanol and n-hexane, reduced the solvent, filtered, washed with 5mL ether and 5mL cold ethanol and dried to form precipitate with deep red colour crystals.

Template Synthesis

Fe(II) complex.

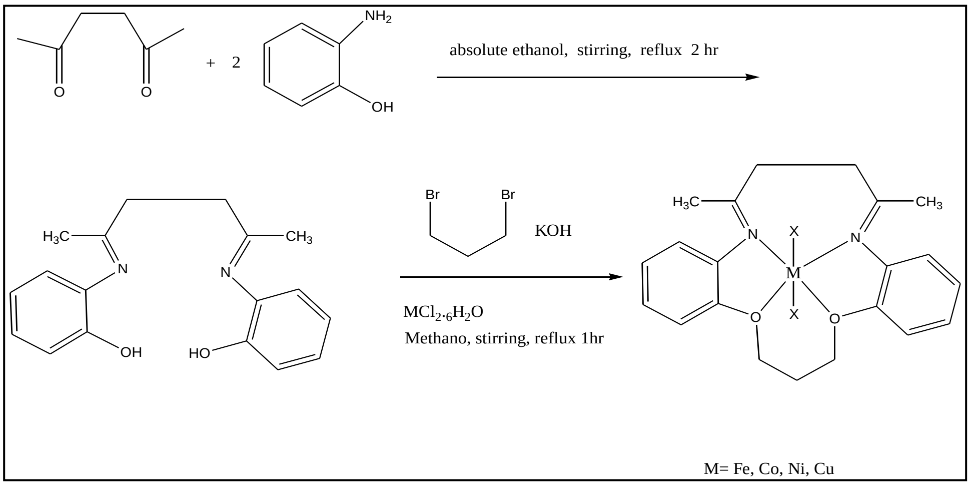
The template reaction method was used for prepare the macrocyclic ligand and their complexes, since, putted the (1.00g, 3.37 mmol.) from the precursor dissolved in 20 mL methanol in round bottomed flask, the two drops of alcoholic KOH was added, then the (0.79g, 3.37 mmol.) from $FeCl_2.6H_2O$ dissolve in 10 mL methanol and (0.32 mL, 3.37 mmol.) from 1,3-dibromopropane are added together as one pot reaction, the mixture solution refluxed for 1.5 hours at about 70 ^{0}C. The deep brown precipitate was obtained, cooled to the room temperature; the solvent was reduced, filtered, washed and dried to gave the titled complex.

Co(II), Ni(II), Cu(II) complexes.

The synthesis of Co(II), Ni(II), Cu(II) complexes were prepared in the similar method which that used in the prepared of Fe(II) complex, but the $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.6H_2O$ are instead of $FeCl_2.6H_2O$. with the proper equivalent quantities.

Results and Discussion

The template reaction and precursor were carried out through the condensation reaction of 2,5-heaxanedione and *O*-hydroxyaniline and the resulted compound was reacted with metal ions and 1,3-dibromopropane to form the complexes. The overall reaction was summarised in the Scheme 2, the prepared compounds were characterised by FT-IR, UV-Vis, HNMR spectroscopy, solubility, molar conductivity, magnetic susceptibility measurments. Table 1. and Table 2.



Scheme 2 route synthesis of precursor and complexes

FT-IR Spectra:-

The FT-IR spectrum of the precursor Fig. (1) displays the characteristic bands at 3638 cm^{-1} attributed to the ν(O-) stretching of hydroxyl groups which that attached to the aromatic ring, while the ν(C=N) stretching of isomethine group appeared at (1625 cm^{-1}). The bands at(2951 cm^{-1}) and 3030 cm^{-1} assigned to ν(C-H) stretching of aliphatic and aromatic groups respectively. While the 1494 cm^{-1} and 1408 can be attributed to the ν(C=C) and ν(C-O) stretching respectively. The FT-IR spectrum of Fe(II) complex Fig. (2) Appears the absence of the band at 3638 cm^{-1} attributed to the ν(O-H) stretching of hydroxyl groups in the free compound (precursor). Indicating to the binding between the 1,3-dibromopropane with the phenolic hydroxyl groups(23). While the shifting to lower frequency at 1600 cm^{-1} for ν(C=N) stretching iminic group, This shifting can be attributed to the delocalisation of the electron density of the metal ion in the π-system of the ligand (HOMO → LUMO) [where HOMO= highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital], the band at (1498 cm^{-1}) assigned to ν(C=C) stretching, while the band at (1369 cm^{-1}) assigned to ν(C-O) stretching, the FT-IR spectra of Co(II), Ni(II), and Cu(II) complexes Figs. (3), (4), (5) exhibits the same details which that showed in the Fe(II) complex. The spectra of these complexes appeared new bands at (316 cm^{-1}, 351 cm^{-1}), (365 cm^{-1}, 401 cm^{-1}), (339 cm^{-1}, 399 cm^{-1}) and (402 cm^{-1}, 435 cm^{-1}) due to the ν(M-N) and ν(M-O) stretching for Fe(II), Co(II), Ni(II), and Cu(II) complexes respectively. And the ν(M-Cl) stretching appeared at the range (220-290 cm^{-1})(24).

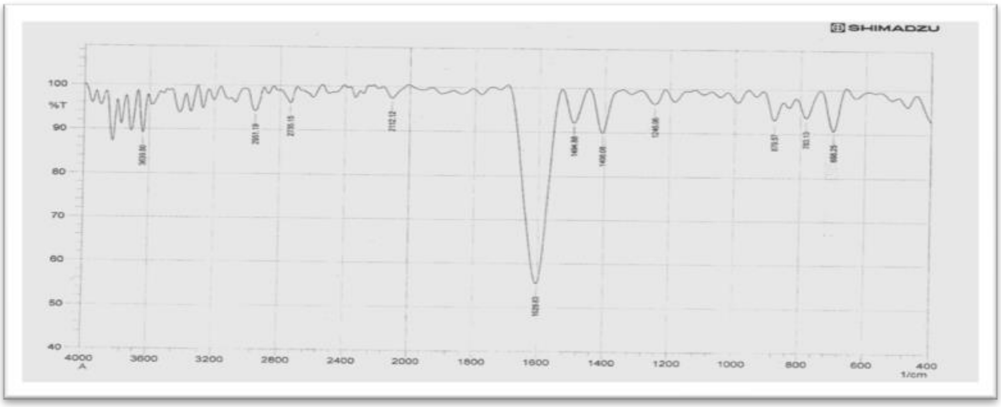


Fig. 1 FT-IR spectrum for precursors

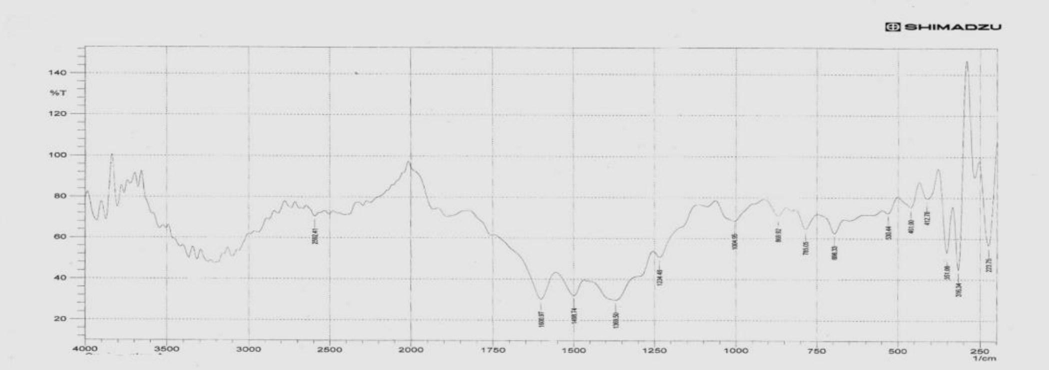


Fig.2 FT-IR spectrum for Fe Complex

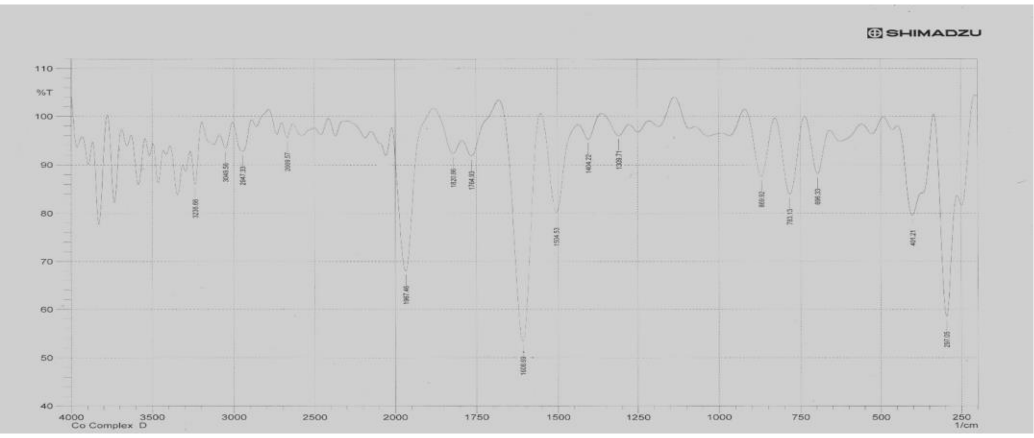


Fig.3 FT-IR spectrum for Co Complex

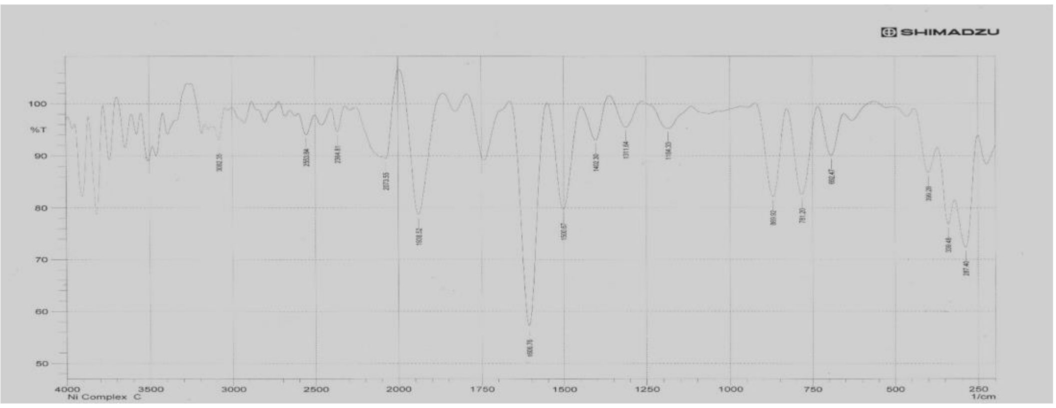


Fig.4 FT-IR spectrum for Ni Complex

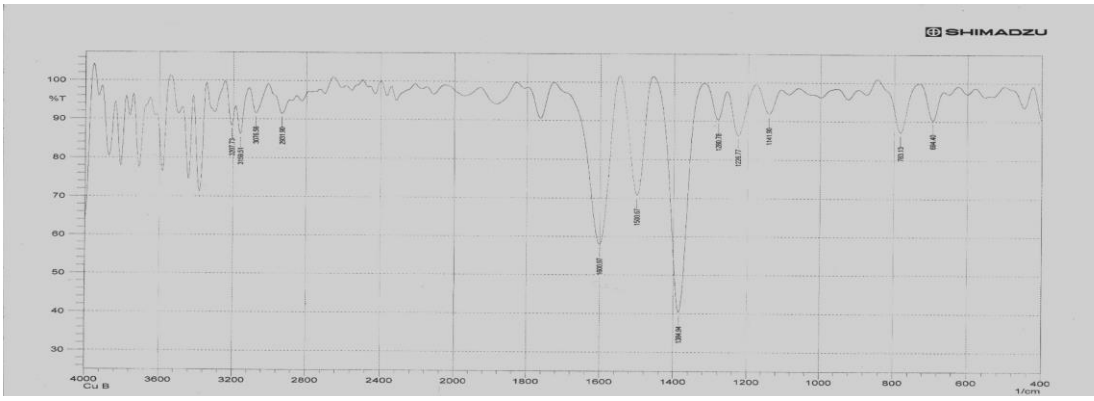


Fig.5 FT-IR spectrum for Cu Complex

UV-Vis spectra

The electronic spectra of the precursor and the template complexes as macro cyclic complexes Figs. (6),(7),(8),(9),(10) for precursor, Fe(II), Co(II), Ni(II), and Cu(II) complexes respectively. Displayed the characteristic peaks, since, the precursor showed the peaks at 234 nm and 280 nm attributed to the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ respectively. While the Fe(II) complex exhibited the a weak peak at 485 nm due to the d-d transition type $^5T_2g \rightarrow {}^5Eg$, Co(II) complex appeared peaks at 467, 555 nm due to the d-d transition type $^4T_1g \rightarrow {}^4T_1g^{(P)}$ and $^4T_1g \rightarrow {}^4T_2g^{(F)}$ respectively, Ni(II) complex displayed the peaks at 655 nm, 740 nm, 785 nm assigned to the d-d transitions type $^3A_2g \rightarrow {}^3T_1g^{(P)}$, $^3A_2g \rightarrow {}^3T_1g^{(F)}$, and $^3A_2g \rightarrow {}^3T_2g^{(F)}$, respectively and the Cu(II) complex appeared the peak at 675 nm due to the d-d transition type $^2Eg \rightarrow {}^2T_2g$ and shoulders at 445nm and 590 nm due to the Jahn-Tellar effect. These results it is more agreement with the previous studies which showed with octahedral geometry. The Ultra Violet region showed the charge transfer and ligand field of the complexes(25).

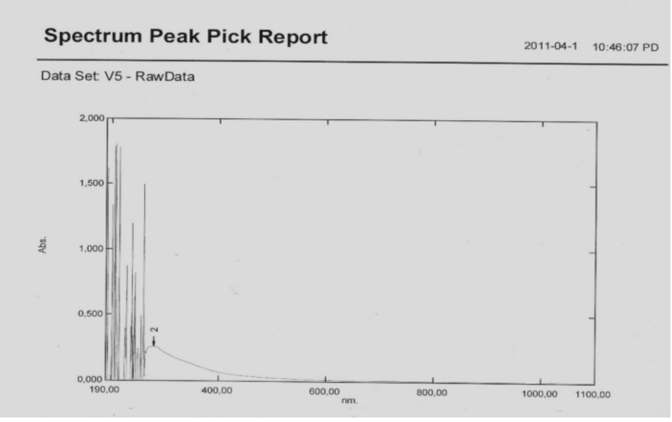


Fig.6 UV-Vis spectrum for precursor

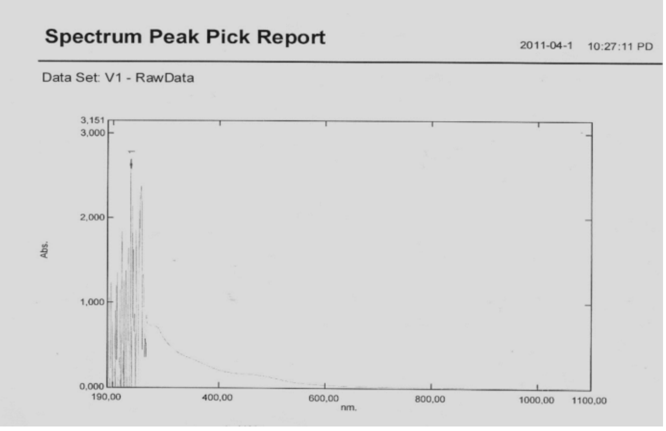


Fig.7 UV-Vis spectrum for Fe complex

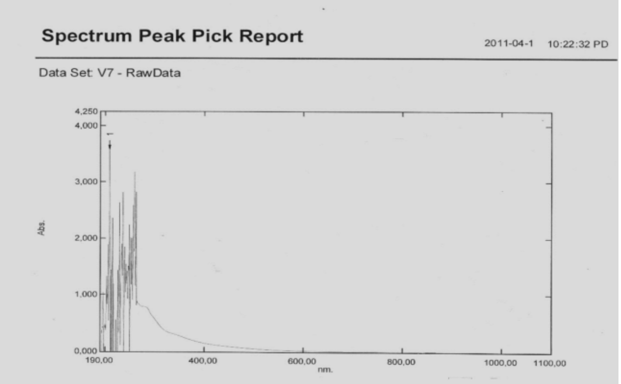


Fig.8 UV-Vis spectrum for Co complex

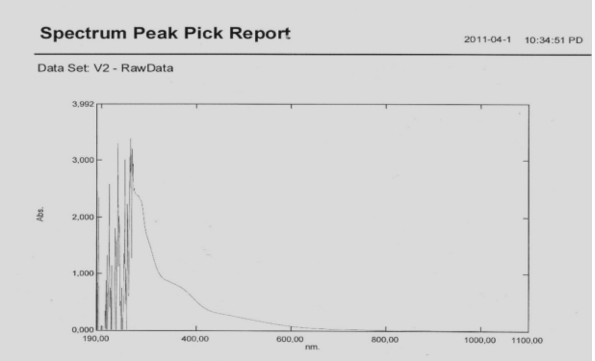


Fig.9 UV-Vis spectrum for Ni complex

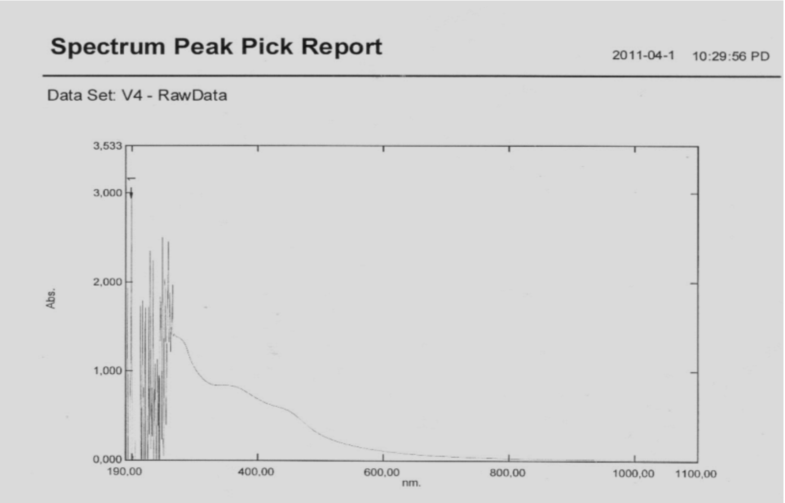


Fig. 10 UV-Vis spectrum for Cu complex

^{1}H NMR Spectra

The H-NMR spectra of the precursor in DMSO-d^6 Fig. (11), , the precursor spectrum exhibited the chemical shift at (δ= 9.97 ppm) due to the phenolic (O-H) protons, the signals between the range (δ= 7.72 ppm - δ= 6.56 ppm) attributed to the aromatic ring protons, the ethyl groups appears the chemical shifts at (δ= 3.37 ppm), while the methyl groups shows the signals at (δ= 1.57 ppm)(23). The signal at (δ= 2.49 ppm) due to the solvent dimethysulfoxide-d^6.

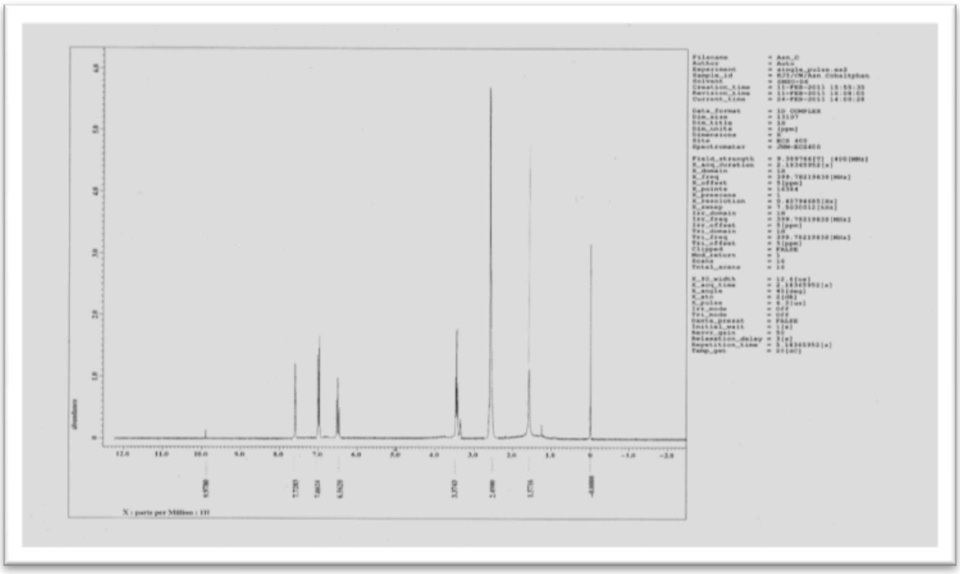


Fig. 11 ^{1}H-NMR spectrum of prcursor

Magnetic susceptibility and conductivity

The magnetic measurements of complexes shows all the complexes are paramagnetic with the 4.88 BM, 4.62 BM, 3.11 BM and 1.71 BM for Fe(II), Co(II), Ni(II), and Cu(II) complexes respectively(26). While the molar conductivity of the complexes (27) was recorded in DMF solvent appears the complexes are electrolyte with 2:1 ratio. Supported with octahedral geometry for complexes.

Table (1) the solubility of compounds

Comp.	*Water*	*DMSO*	*DMF*	*MeOH*	*Ether*	*Benzene*
Pre.	-	+	+	/	-	-
Fe complex	-	+	+	-	-	-
Co complex	-	+	+	+	-	-
Ni complex	-	+	+	/	-	-
Cu complex	-	+	+	+	-	-

(+) completely miscible,(-) incompletely miscible,(/) partially miscible

Table (2) the physical properties of compounds

Comp.	*Colour*	*Magnetic moment BM*	*Conductivity*	*M.P.*
Pre.	*yellow*	-	-	*301-303*
Fe complex	*Purple*	*4.88*	*145*	*314-316*
Co complex	*Brown*	*4.62*	*162*	*332-334*
Ni complex	*Blue*	*3.11*	*125*	*326-328*
Cu complex	*Blue*	*1.71*	*133*	*308-310*

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