

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/340607316>

# STRUCTURAL STUDY OF COMPLEXES FROM HEXAFLUOROACETYLACETONE, PYRAZOLE, AND ITS PYRAZOLE DERIVATIVE WITH SOME METALS BY FT-IR, AND <sup>1</sup>H-NMR

Article · March 2020

DOI: 10.52571/PTQ.v17.n34.2020.780\_P34\_pgs\_756\_768.pdf

CITATIONS

0

READS

564

6 authors, including:



**Jassim Abas Al-Hilfi**

University of Misan

15 PUBLICATIONS 37 CITATIONS

[SEE PROFILE](#)



**Tahseen Saddam Fandi Al-Mathkuri**

University of Misan

11 PUBLICATIONS 6 CITATIONS

[SEE PROFILE](#)



**Luma M. Ahmed**

University of Kerbala

82 PUBLICATIONS 544 CITATIONS

[SEE PROFILE](#)



**Zaidoon Jawad**

University of Misan

14 PUBLICATIONS 32 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Synthesis, Characterization of Fe<sub>2</sub>O<sub>3</sub> and Application on colored solution [View project](#)



Depressed the poisoning of complexes [View project](#)

ESTUDO ESTRUTURAL DE COMPLEXOS DE HEXAFLUOROACETILACETONA, PIRAZOL E DERIVADOS DE PIRAZOL COM ALGUNS METAIS POR FT-IR E <sup>1</sup>H-RMNSTRUCTURAL STUDY OF COMPLEXES FROM HEXAFLUOROACETYLACETONE, PYRAZOLE, AND ITS PYRAZOLE DERIVATIVE WITH SOME METALS BY FT-IR, AND <sup>1</sup>H-NMRدراسة تركيبية من معقدات الهكسوفلورواسيتايل اسيتون، البيروزول، و مشتق البيروزول مع بعض الفلزات بواسطة FT-IR و <sup>1</sup>H-NMRJassim Abas Al-Hilfi<sup>1\*</sup>, Zaidoon Jawad Kahdim<sup>1</sup>, Tahseen Saddam Fandi<sup>1</sup>, and Luma M. Ahmed<sup>2</sup><sup>1</sup>Department of Chemistry, College of Science, University of Misan, Maysan, Iraq<sup>2</sup>Department of Chemistry, College of Science, University of Kerbala, Kerbala, Iraq

\* Correspondence author

e-mail: jassimal-hilfi@uomisan.edu.iq

Received 12 January 2020; received in revised form 28 February 2020; accepted 11 March 2020

## RESUMO

As formações complexas em série de níquel (II) ou cobalto (III) com hexafluoroacetilacetona, pirazol, 3,5-dimetilpirazol e 3,5-bis(trifluorometil)-1H-pirazol foram preparadas. O primeiro passo da reação incluiu a síntese do complexo a partir da utilização de hexafluoroacetilacetona como um ligante com Co(III) ou Ni(II) um metal, de spin alto com doação de  $\pi$  e forma enol do ligante. O complexo formado foi identificado por FT-IR, espectroscopia de <sup>1</sup>H-RMN e cálculo de suscetibilidade magnética. Considerando que o segundo passo para a produção do complexo dependia da mistura de água com pirazol e usando-os como ligantes com Co(III) ou Ni(II) um metal, de spin alto com doação e um átomo de nitrogênio aromático é doador do ligante. Na terceira etapa, o complexo foi produzido misturando água com 3,5-bis(trifluorometil)-1H-pirazol como ligante com Co(III) ou Ni(II) um metal, de spin baixo. A investigação dos complexos preparados e dos ligantes utilizados foi realizada comparando os resultados de espectroscopia de <sup>1</sup>H-RMN de FT-IR. Além disso, o cálculo da suscetibilidade magnética também foi empregado. Os resultados da espectroscopia de <sup>1</sup>H-RMN e suscetibilidade magnética provaram que os complexos produzidos são diamagnéticos, quando o ligante inclui o grupo CF<sub>3</sub>. Ao mesmo tempo, os complexos produzidos são paramagnéticos, quando o ligante não contém o grupo CF<sub>3</sub>, que é formado com a mistura de água e 3,5-dimetilpirazol como ligante, ou água e pirazol como ligante, com Co(III) ou Ni(II) como metal. Todos os ligantes nos complexos paramagnéticos possuíam um átomo doador e outro o átomo receptor no pirazol que é um átomo de nitrogênio aromático. Portanto, todos os complexos de alta rotação preparados não eram evidentes no espectro de <sup>1</sup>H-RMN, porque os picos parecem ninhados que, devido ao alto tempo de relaxamento de <sup>1</sup>H-RMN de T<sub>1</sub>, e a investigação resultou em dois picos de atribuição. Esse comportamento é uma atitude para ocorrer o fenômeno da forma cetona e da forma enol usando os espectros de <sup>1</sup>H-RMN, e é um acoplamento evidente entre o átomo de hidrogênio ou carbono com um átomo de flúor.

**Palavras-chave:** hexafluoroacetilacetona, complexos de Co(III) e Ni(II), espectros de FT-IR e <sup>1</sup>H-RMN.

## ABSTRACT

The series complex formation nickel(II) or cobalt(III) with hexafluoroacetylacetone, pyrazole, 3,5-dimethylpyrazole, and 3,5-bis(trifluoromethyl)-1H-pyrazole were prepared. The first reaction step included the synthesis of the complex using hexafluoroacetylacetone as a ligand with Co(III) or Ni(II), metals with high spin with  $\pi$  donate and enol-form of the ligand. This formed complex was identified by FT-IR, <sup>1</sup>H-NMR spectroscopy, and magnetic susceptibility calculation. Whereas, the second reaction step to produce the complex depended upon mixing water and pyrazole and using it as ligands with Co(III) or Ni(II) a metal, which is a high spin with one donate and the another is aromatic nitrogen atom in a ligand. In the third reaction step, the complexes were produced by mixing water with 3,5-bis(trifluoromethyl)-1H-pyrazole as a ligand with Co(III) or Ni(II) as low spin

metal. The analysis of these prepared complexes and their used ligands were done by comparing the results using  $^1\text{H-NMR}$  and FT-IR spectroscopies. Besides, the magnetic susceptibility calculation was also employed. The results of  $^1\text{H-NMR}$  spectroscopy and magnetic susceptibility proved that the produced complexes are diamagnetic when the ligand includes the  $\text{CF}_3$  group. At the same time, the produced complexes are paramagnetic, when the ligand without the  $\text{CF}_3$  group, which is formed the mixture of water and 3,5-dimethylpyrazole as ligand or water and pyrazole as a ligand with Co(III) or Ni(II) as metal. All the ligands in the paramagnetic complexes were one donate, and another the donated atom in pyrazol is an aromatic nitrogen atom. Therefore all prepared high spin complexes were not evident in the  $^1\text{H-NMR}$  spectrum because the peaks appear broad that due to high  $T_1$  relaxation  $^1\text{H-NMR}$  time, and the investigation turned out two assignment peaks. This behavior is an attitude to happen the ketone form and enol form phenomenon by using  $^1\text{H-NMR}$  spectra, and its an evident assignment coupling between hydrogen or carbon atom with a fluorine atom.

**Keywords:** hexafluoroacetylacetone, complexes Co(III) Ni(II), FT-IR, and  $^1\text{H-NMR}$  spectra.

## المخلص:

حضرت سلسلة من معقدات النيكل(II) أو الكوبلت(III) مع هكسوفلورواسيتايل اسيتون، والبيرازول، و 3،5-ثنائي مثيل بيرازول، و 3،5-بس(تراي فلورومثيل)-1-هيدروجين-البيرازول. تضمنت خطوة التفاعل الاولى تحضير المعقد باستخدام الليكاند هكسوفلورواسيتايل اسيتون مع فلز الكوبلت(III) أو النيكل(II)، حيث يكون سلوك الليكاند عالي البرم ومانح لمزدوجين الكترونيين (ثنائي المنح) وعلى شكل اينول فورم. شخّصت المعقدات المتكونة بواسطة مطيافية FT-IR و مطيافية  $^1\text{H-NMR}$  وحسابات الحساسية المغناطيسية. بينما تضمنت الخطوة الثانية، تحضير معقد بالأعتماد على استخدام مزيج من الماء والبيرازول كلكاندات مع فلز الكوبلت(III) أو النيكل(II)، إذ تكون الفلزات عالية البرم وتحوي ليكاند مانح لزوج إلكتروني وليكاند اخر تكون فيه الذرة المانحة ذرة النيتروجين الاروماتية. في الخطوة الثالثة، حضرت المعقدات من مزيج متكون من تفاعل الماء و 3،5-بس(تراي فلورومثيل)-1-هيدروجين-بيرازول كاليكاندات مع فلز الكوبلت(III) أو النيكل(II) واطئة البرم. تم تشخيص هذه المعقدات المحضرة من الليكاندات المستخدمة عن طريق مقارنة النتائج بواسطة مطيافية  $^1\text{H-NMR}$  ومطيافية FT-IR. بالإضافة الى ذلك فقد استخدمت حسابات الحساسية المغناطيسية لهم. برهنت نتائج مطيافية  $^1\text{H-NMR}$  والحساسية المغنايسية بأن المعقدات المتكونة هي دايا مغناطيسية (الفلز واطيء البرم)، عندما يحوي الليكاند على مجموعة  $\text{CF}_3$ ، بينما تكون المعقدات الناتجة بارا مغنايسية (الفلز عالي البرم)، عندما لا يحوي الليكاند على مجموعة  $\text{CF}_3$ ، والتي تتكون من مزيج من الماء و 3،5-بس(تراي فلورومثيل)-1-هيدروجين-البيرازول كلكاند او ليكاند من الماء والبيرازول مع فلز الكوبلت(III) أو النيكل(II). تكون جميع الليكاندات في المعقدات البارامغناطيسية مانحة لمزدوج إلكتروني واحد، والآخر في البيرازول فان ذرة النيتروجين الاروماتية هي الذرة المانحة. لذلك تكون جميع المعقدات عالية البرم المحضرة غير واضحة في طيف  $^1\text{H-NMR}$ ، لظهور حزم عريضة والتي تُعزى لزمان الاسترخاء السريع للبروتونات في الرنين النووي المغناطيسي، وشخّصت اشارتين مهمة. عُزّي هذا السلوك الى حدوث ظاهرة الكيتون فورم والينول فورم باستخدام اطياف  $^1\text{H-NMR}$ ، والتي اعطت ازدواج مميز لذرة الهيدروجين او ذرة الكربون مع ذرة الفلور.

**الكلمات المفتاحية:** هكسوفلورواسيتايل اسيتون، معقدات الكوبلت(III) النيكل(II)، مطيافية FT-IR و مطيافية  $^1\text{H-NMR}$ .

## 1. INTRODUCTION

Hexafluoroacetylacetone was used as a chelating agent in this work. It has been widely used as a chelating agent for the determination of neptunium and plutonium and the extraction of lanthanides and actinides. The IUPAC name of hexafluoroacetylacetone is 1,1,1,5,5,5-hexafluoro-2,4-pentanedione. It was one of the  $\beta$ -diketone derivatives in which two  $\text{CF}_3$  groups substituted  $R_1$  and  $R_2$   $\beta$ -diketone ligands have been extensively studied in coordination as well as organometallic chemistry for several decades and are the precursors for various heterocyclic compounds such as pyrazole and imidazole. The presence of electron-withdrawing groups, such as  $\text{CF}_3$  groups, favors the enol form (Burdett and Rogers, 1964). When four or more fluorine atoms are present in the molecule, the enolization is complete (Pashkevich *et al.*, 1981). For instance, 100% of the molecules of hexafluoroacetylacetone are in the enol form. Also, phenyl groups favor the enol form (Reid J.C, Calvin, 1950). It was already about 100% of

the molecules of dibenzoylmethane are in the enol form. For their compounds, the lower the polarity of the solvent, the higher is the percentage of the enol form. In  $\text{CCl}_4$ , 94% of the acetylacetone molecules are present in the enol form, whereas, in acetonitrile, this value is reduced to 36%. The amount of enol form decreases with increasing temperatures. As the degree of enolization increases, the acidity of the enol proton decreases (Hammond *et al.*, 1959). In the case of unsymmetrically-substituted  $\beta$ -diketones, two different enol forms are possible (Lowe Jr. and Ferguson, 1965). It has been shown that benzoylacetylacetones (with different substituents in the *para*-position of the phenyl group) are enolized towards the phenyl group. The acidity of the  $\beta$ -diketone depends on the substituents. Because of the presence of the two carbonyl groups, the proton on the  $\alpha$ -carbon is quite acidic, and relatively weak bases can remove it. However, by compulsion of acetylacetone and benzoylacetylacetone, the enolization is accessed towards the phenyl group, but in the flour acetylacetone, it accesses the  $\text{CF}_3$  group. In general, the techniques that

can be used in studying the enolization and tautomerism in  $\beta$ -dicarbonyl compounds are  $^1\text{H-NMR}$ , FT-IR, and U.V. spectrophotometry. Nevertheless, the most powerful method is  $^1\text{H-NMR}$ .  $\beta$ -diketone and their metal complexes have several applications in different fields. The rare-earth  $\beta$ -diketones are used as  $^1\text{H-NMR}$  shift reagents (Morrill, 1986; Hinckley, 1969). Ketoamines and their metal(II) complexes continue to attract attention because of their unique catalytic and coordination properties (Schrock *et al.*, 1999; Graf *et al.*, 1999; Guérin *et al.*, 1998; Stabnikov *et al.*, 2003; Baidina *et al.*, 2004a; Baidina *et al.*, 2003).  $\beta$ -diketones can be used, e.g., for the preparation of ketoimines (by condensation with amines), thioketones, and various heterocyclic compounds (e.g., pyrimidine derivatives) (Baidina, 2004b).

## 2. MATERIALS AND METHODS

### 2.1 preparation of tris(hexafluoroacetylaceton)cobalt(III) and the bis (hexafluoroacetylaceton)nickel(II) as first reaction step

The tris(hexafluoroacetylaceton)cobalt(III) or bis(hexafluoroacetylaceton)nickel(II) were prepared as in the Equation 1 according to the literature with changed in precursor materials (Sharma *et al.*, 2003; Woods *et al.*, 2004). It was altered the amount of reactants and reflux times. Exactly (29.317 mg, 0.1177 mmol) from  $\text{Co}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  or (43.92 mg, 0.1765 mmol) from  $\text{Ni}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 5 mL ethanol and 1 mL acetic acid, and then added to the hexafluoroacetylaceton (73.5 mg, 0.353 mmol). The suggested structure of the product is shown in Figure 3. It was confirmed by FT-IR,  $^1\text{H-NMR}$  spectroscopy, and magnetic susceptibility calculated.

### 2.2 preparation of triaquatripyrazole cobalt(III) or diaquadipyrazole nickel(II) as second reaction step

The triaquatripyrazolecobalt(III) or diaquadipyrazolenickel(II) were prepared as in the Equation 2 according to the literature with changed in precursor materials (Sharma *et al.*, 2003; Woods *et al.*, 2004), amount of reactants, and reflux times.  $\text{Co}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Ni}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  (165.74 mg, 0.66 mmol or 248.86 mg, 1 mmol respectively) in 14 mL ethanol was added to the pyrazole (136 mg, 2 mmol). The suggested structure of the product is presented in Figures 5 and 6. The structure was confirmed by FT-IR spectroscopy, and the

magnetic susceptibility was calculated.

### 2.3 Preparation of 3,5-bis(trifluoromethyl)-1H-pyrazole

The compound was prepared as in Equation 3, according to the literature with changes in the precursor materials (Clark, 2010; Al-Mathkuri *et al.*, 2018), amount of reactants, rate of solvents, and reflux times. Hexafluoroacetylaceton (780.22 mg, 3.75 mmol) in 14 mL ethanol, toluene, and THF were added to the hydrazine (120.19 mg, 3.75 mmol). The suggested structure of the product is shown in Figure 8. It was confirmed by FT-IR. spectroscopy and the magnetic susceptibility was calculated.

### 2.4 Preparation of the diaquabis(hexafluoroacetylaceton)nickel(II) as the third reaction step

The diaquabis(hexafluoroacetylaceton)nickel(II) was prepared in Equation 4 according to the literature with a change in the precursor materials (Sharma *et al.*, 2003; Woods *et al.*, 2004), amount of reactions, and reflux times.  $\text{Co}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Ni}(\text{CH}_3\text{COOH})_2 \cdot 4\text{H}_2\text{O}$  (83.43 mg, 0.335 mmol or 483.86 mg, 1.944 mmol respectively) in 15 mL ethanol was added to the 3,5-bis(trifluoromethyl)-1H-pyrazole or 3,5-methylpyrazole (338.0 mg, 1.6598 mmol or 560 mg, 5.833 mmol respectively). One suggests that the structure of the product is shown in Figure 8. It was confirmed by FT-IR,  $^1\text{H-NMR}$  spectroscopy, and the magnetic susceptibility was calculated.

## 3. RESULTS AND DISCUSSION:

The  $^1\text{H-NMR}$  spectrum of a hexafluoroacetylaceton sample is shown in Figure 1. The spectrum in DMSO as a solvent at 0 °C using TMS as an internal reference. The appearance of the single peak (significant peak) at 6.480 ppm was assigned to a vinylic proton, the peak at 2.055 ppm attribute to a  $\text{CH}_2$  keto-form, the peak at 10.868 ppm attributed to a OH enol-form (Al-Hilfi *et al.*, 2019).

All prepared complexes were magnetic susceptibility to figure out the physics of the magnetic behavior, and the results were paramagnetic of all prepared complexes from pyrazole and 3,5-dimethylpyrazole as ligands while it was diamagnetic of all prepared complexes from 3,5-bis(trifluoromethyl)-1H-pyrazole, therefore the hybridization of the prepared complexes from pyrazole and 3,5-

dimethylpyrazole as ligands with Co or Ni as a metal was  $sp^3d^2$  and  $sp^3$  respectively, while it is of prepared complexes from 3,5-bis(trifluoromethyl)-1H-pyrazole as a ligand with Co or Ni as a metal was  $d^2sp^3$  and  $dsp^2$  respectively. The  $^{13}C$ -NMR spectrum of a hexafluoroacetylacetone sample is shown in Figure 2. The spectrum of hexafluoroacetylacetone in DMSO as a solvent at 0 °C with the using TMS as the internal reference. The spectrum shown three peaks (because coupling with fluoride) at range 26.288-35.144 ppm assigned to  $CH_2$  ketone-form, multi peaks (because coupling with fluoride) at range 91.704-95.238 attributed to CH enol-form, carbon of CH enol-form splitting more than carbon of  $CH_2$  keto-form with fluoride are because enol-form is resonance system more than is resonance system keto-form, and enol-form is two forms a structure of hexafluoroacetylacetone, while one form is keto-form. Multi peak around at 124 ppm attributed to  $CF_3$  groups, multi peaks around at 159 ppm assigned to carbonyl groups. Figures 1 and 2, respectively, confirm the ligand of the starting material. At Tables 1 and 2, some spectral data of the starting material ligand and its complex (Walmsley and Walmsley, 2005; Pavia *et al.*, 2009).

At Figure 4, the  $^1H$ -NMR spectrum of the pyrazole sample, the spectrum appeared triplet peak at 6.369 ppm due to proton number 8, doublet peak at 7.657 ppm assigned to protons number 7 and 9, whereas proton of NH group disappeared because tautomerism between two nitrogen atoms while its appeared in spectra 6 and 7 of two complexes prepared from pyrazole as a ligand with nickel or cobalt as a metal respectively, and appeared shifting in complexes spectra in Table 3. Table 3 appears different between ligand with complexes more than Table 1 may be attributed to the lone pair donor of the nitrogen atom in aromatic while in Table 1 was aliphatic. Therefore it may be assigned to the aromatic system deflect, and the  $^1H$ -NMR spectra of complexes were high resolution of protons coupling may because of shift reagent of metals (Pavia *et al.*, 2009). At Table 4, appears triplet peak at 6.867, 7.038, 7.208 ppm because of the coupling between the proton with fluoride attributed to the aromatic proton of pyrazole while its peak appears brood peak at 7.473 ppm in the complex.

The results in Figures (11-13) and Table 5 revealed that the complex of 3,5-bis(trifluoromethyl)-1H-pyrazole with Ni(II) was successfully prepared by the analysis of the positions of the peaks (Silverstein and Bassler,

1962; Nakamoto, 1970; CHACÓN *et al.*, 2018; Santorum *et al.*, 2018). The shift in the peaks in Table 5 is proven that the complex with Ni(II) was prepared from 3,5-bis(trifluoromethyl)-1H-pyrazole as a ligand with nickel(II) (Silverstein and Bassler, 1962; Nakamoto, 1970).

#### 4. CONCLUSIONS:

In the first reaction step, the prepared complexes were paramagnetic. Hence the complex formed from nickel as a metal whose hybridization was  $sp^3$ , and whereas the complex formed from cobalt as a metal whose hybridization was  $sp^3d^2$ . The prepared complexes were  $\pi$  donating, their two bonds between the ligand and the transition metal are one bond covalent a charge, and two bonds donate.

In the second reaction step, the prepared complexes were paramagnetic. Hence the complex formed from nickel as a metal whose hybridization was  $sp^3$ , and whereas the complex formed from cobalt as a metal whose hybridization was  $sp^3d^2$ . The prepared complexes contained from one donate ligand and another donated ligand (one bond donated for neutralizing the metal) between the ligand and the transition metal.

In the third reaction step, the prepared complexes were diamagnetic. Hence the complex formed from nickel as a metal whose hybridization was  $dsp^2$ , and whereas the complex formed from cobalt as a metal whose hybridization was  $d^2sp^3$ .

The prepared complexes consisted of one donate ligand and another donated ligand (one bond donate as neutral of metal) between the ligand and the transition metal.

The FT-IR spectra indicated that the complex between 3,5-bis(trifluoromethyl)-1H-pyrazole and Ni(II), were successfully synthesized.

#### 5. ACKNOWLEDGMENTS:

The authors wish to acknowledge the College of Science staff at University of Misan in supporting this work in their laboratories.

#### 6. REFERENCES:

1. Burdett J. L., Rogers M. T. *Journal of the American Chemical Society*. **1964**, 86(11):2105-9.

2. Pashkevich K. I., Saloutin V. I., Postovskii I. Y. *Russian Chemical Reviews*. **1981**,50(2):180.
3. Reid J. C., Calvin M. *Journal of the American Chemical Society*. **1950**, 72(7):2948-52.
4. Hammond G. S., Borduin W. G., Guter G.A. *Journal of the American Chemical Society*. **1959**, 81(17):4682-6.
5. Lowe Jr J. U., Ferguson L. N. *The Journal of Organic Chemistry*. **1965**, 30(9):3000-3.
6. Morrill T.C. Lanthanide shift reagents in stereochemical analysis. New York: VCH; **1986**.
7. Hinckley C. C. *Journal of the American Chemical Society*. **1969**, 91(18):5160-2.
8. Schrock R. R., Seidel S. W., Schrodi Y., Davis W. M. *Organometallics*. **1999**, 18(3):428-37.
9. Graf D. D., Schrock R. R., Davis W. M., Stumpf R. *Organometallics*. **1999**, 18(5):843-52.
10. Guérin F., McConville D. H., Vittal J. J., Yap G. A. *Organometallics*. **1998**, 17(23):5172-7.
11. Stabnikov P. A., Baidina I. A., Sysoev S. V., Vanina N. S., Morozova N. B., Igumenov I.K. *Journal of Structural Chemistry*. **2003**, 44(6):1054-61.
12. Baidina I. A., Zharkova G. I., Pervukhina N. V., Gromilov S.A., Igumenov I. K. *Journal of Structural Chemistry*. **2004a**, 45(4):678-687.
13. Baidina I. A., Gromilov S. A., Zharkova G. I., Stabnikov P. A. *Journal of Structural Chemistry*. **2003**, 44(3):448-56.
14. Baidina I. A., Stabnikov P. A., Vasiliev A. D., Gromilov S. A., Igumenov I. K. *Journal of Structural Chemistry*. **2004b**, 45(4):671-677.
15. Sharma S., Rai A. K., Singh Y. *Phosphorus, Sulfur, and Silicon*. **2003**, 178(11):2457-63.
16. Woods J. A., Osowole A. A., Odunola O. A. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*. **2004**, 34(8):1471-85.
17. Clark, J. Stephen. "Heterocyclic Chemistry." **2010**.
18. Walmsley J. A., Walmsley F. *Journal of the Korean Chemical Society* **2005**, 49(1).
19. Pavia D. L., Lampman G. M., Kriz G. S., Vyvyan J. A. Introduction to spectroscopy. 4<sup>th</sup> edition, Cengage Learning. **2009**, USA.
20. Silverstein R. M., Bassler G. C. *Journal of Chemical Education*. **1962**, 39(11):546.
21. Nakamoto, Kazuo. "Infrared spectra of inorganic and coordination compounds." **1970**.
22. CHACÓN C., HENAO J.A., JAMALIS J., RIVAS P., VELÁSQUEZ W., DELGADO G.E. *Periódico Tchê Químico*. **2018**, 15 (29) :292-299.
23. Santorum N., Fabara A., Pilaquinga F., Ampudia S., Jara E., Meneses L. *Periódico Tchê Químico*. **2018**,15(29):309-18.
24. Al-Hilfi J. A., AL-Furiji H. S., Saleh A. T. *ARCTIC Journal*. **2019**, 72(9):149-163.
25. Al-Mathkuri T. S., Al-Jubori H. M., Saleh A. T. *Oriental Journal of Chemistry*. **2018**, 34(4):2031-42.

**Table 1.** <sup>1</sup>H-NMR chemical shifts in ppm of hexafluoroacetylacetone and complex from hexafluoroacetylacetone as a ligand with cobalt as a metal (Pavia *et al.*, 2009)

Assigned protons	Chemical Shifts of ligand	Chemical Shifts of complex
Vinyl proton	6.48	7.176
Proton CH <sub>2</sub> moiety	2.055	2.397

**Table 2.** <sup>13</sup>C NMR chemical shifts in ppm of hexafluoroacetylacetone and complex from hexafluoroacetylacetone as a ligand with cobalt as a metal (Walmsley and Walmsley, 2005)

Assigned carbons	Chemical Shifts of ligand	Chemical Shifts of complex
The carbon of the CH group	Multi peak around at 94.00	Two peaks at 94.337-94.770
carbon CH <sub>2</sub> group	Three peaks at 26.288-30.435-35.144	33.065
Carbon C=O group	Two peaks at 159.147-159.656	Two peaks at 148.255-207-418

**Table 3.** <sup>1</sup>H-NMR chemical shifts, in ppm, of pyrazole and complex from pyrazole as a ligand with nickel as a metal (number 1) or cobalt as a metal (number 2).

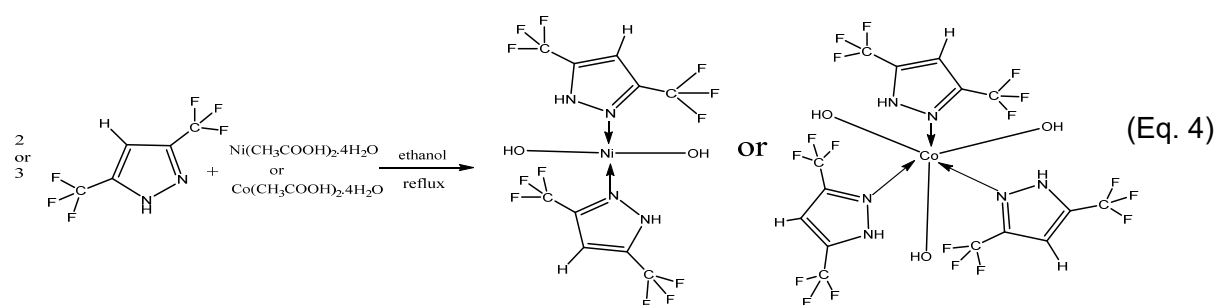
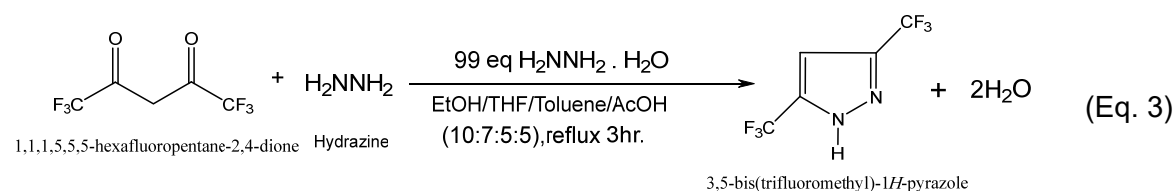
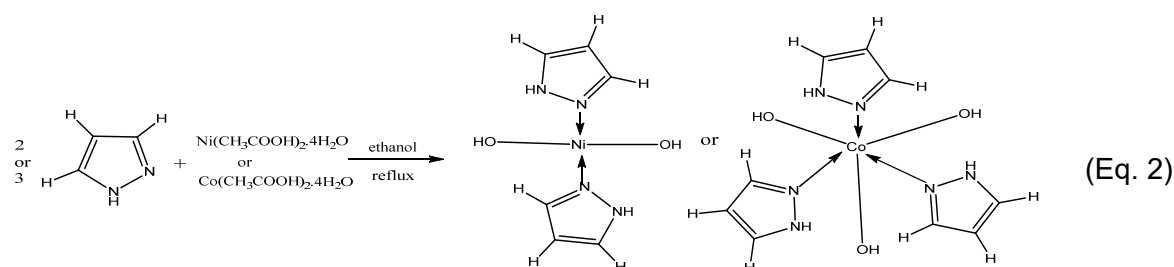
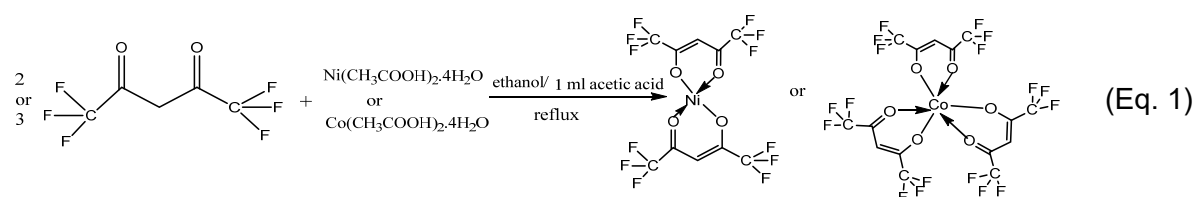
Assigned protons	Chemical Shifts of pyrazole	Chemical Shifts of complex number 1	Chemical Shifts of complex number 2
Proton number 8	6.369	4.007	3.992
Protons number 7 and 9	7.657	4.722	4.676
Proton number 6	12.3	Brood; disappeared	7.335

**Table 4.** <sup>1</sup>H-NMR chemical shifts, in ppm, of 3,5-bis(trifluoromethyl)-1*H*-pyrazole and complex from 3,5-bis(trifluoromethyl)-1*H*-pyrazole as a ligand with nickel as a metal.

Assigned protons	Chemical Shifts of pyrazole	Chemical Shifts of complex
Aromatic proton(triplet peak)	6.867,7.038,7.208	7.473
The proton of the NH group	8.389	10.34

**Table 5.** FT-IR bands in  $\text{cm}^{-1}$  of hexafluoroacetylacetone, 3,5-trimethylpyrazole, and complex from 3,5-bis(trifluoromethyl)-1*H*-pyrazole as a ligand with nickel as a metal.

functional group names assigned	FT-IR bands of hexafluoroacetylacetone	FT-IR bands of pyrazole	FT-IR bands of complex
$\nu(\text{C-F})$ stretching (strong peak)	1138.11-1178.55	-	1136.11
$\nu(\text{C-N})$ stretching (strong peak)	-	1305.85	1242.20
$\nu(\text{C=O})$ stretching	Brood band at 1650	-	-
$\nu(\text{N-H})$ stretching (strong peak)	-	3200.01	Brood band at 3400.62





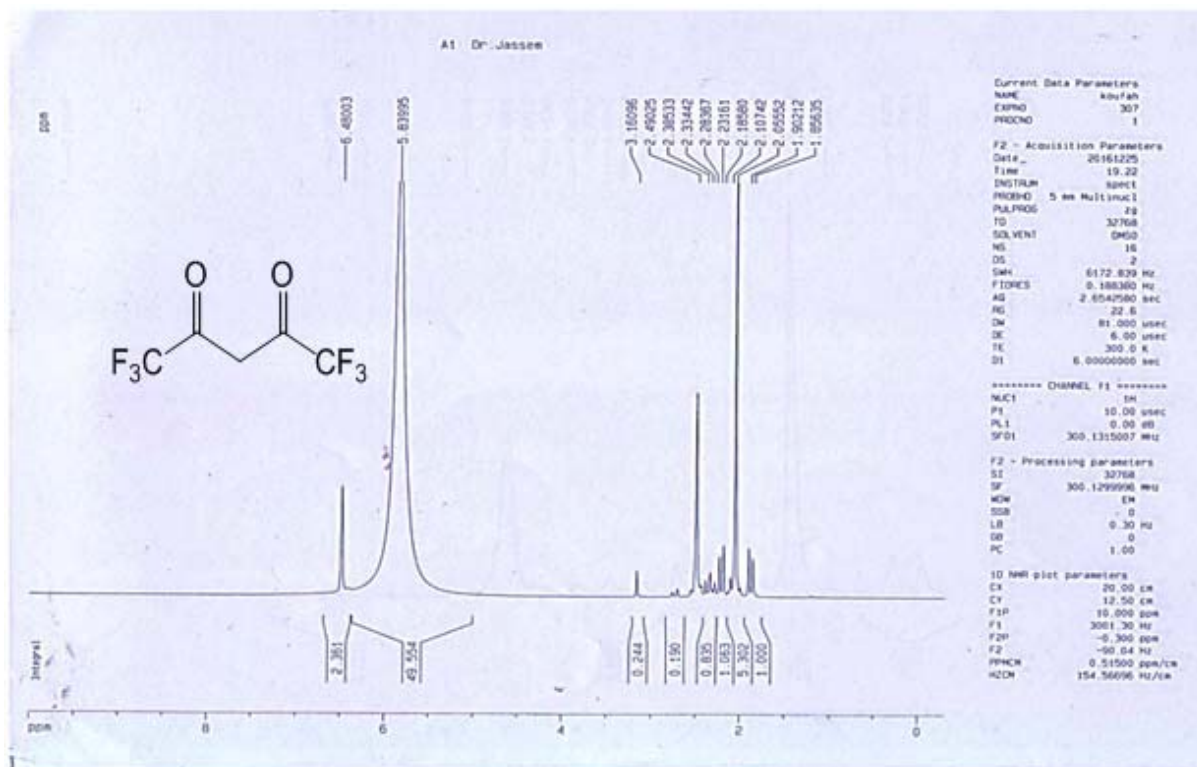


Figure 1. <sup>1</sup>H NMR spectrum of a hexafluoroacetylacetone.

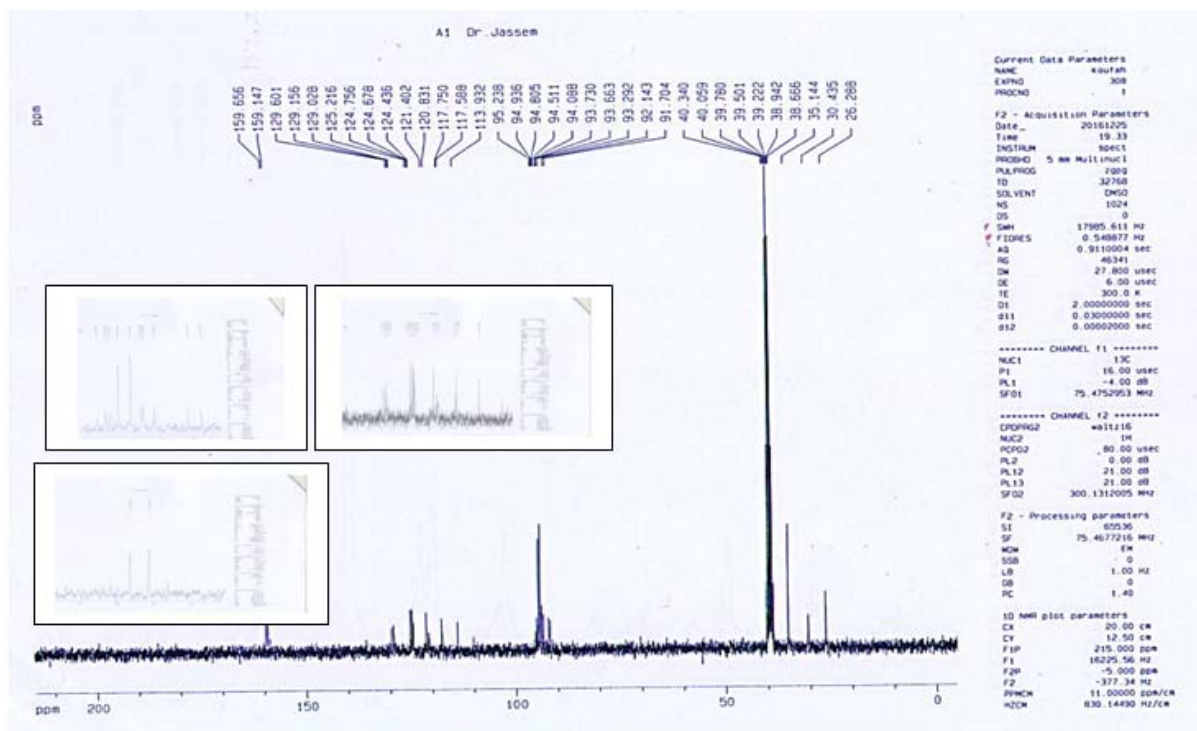
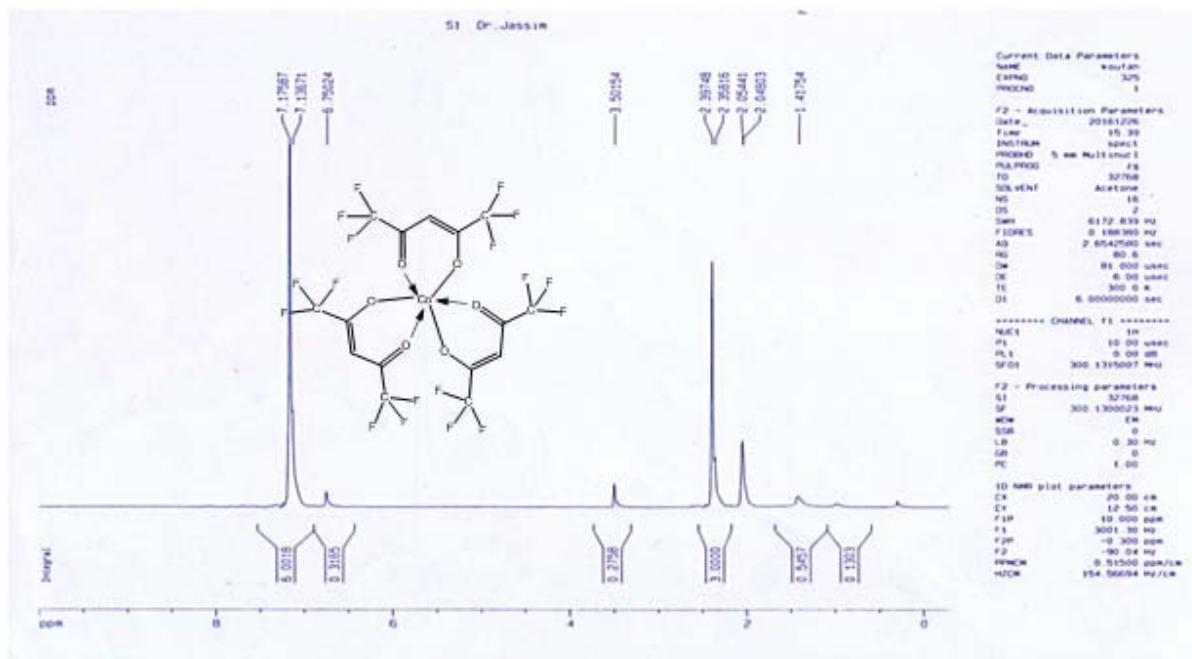
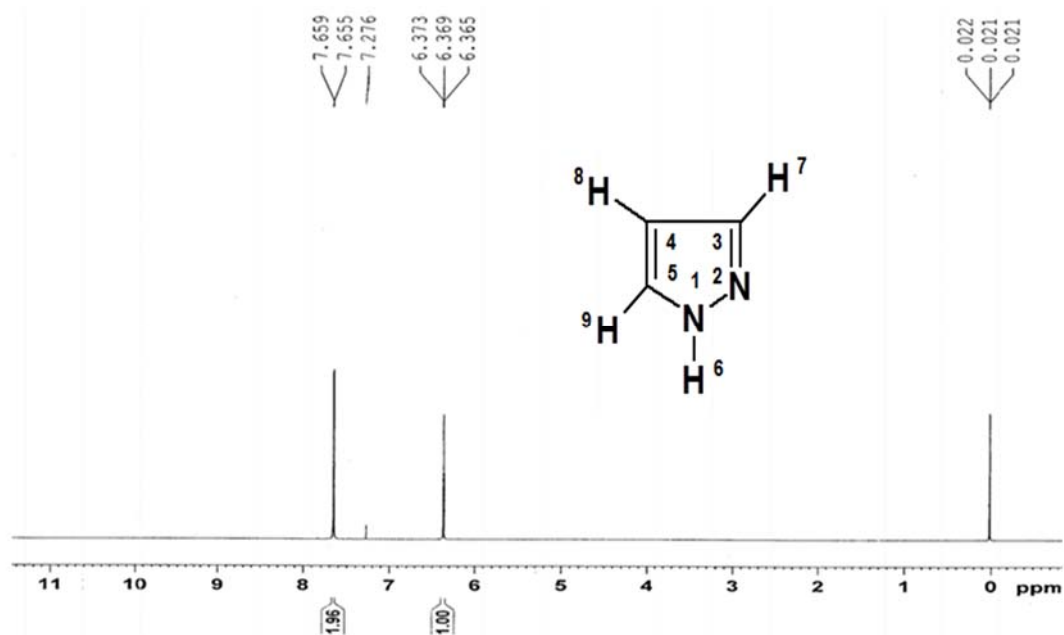


Figure 2. <sup>13</sup>C-NMR spectrum of a hexafluoroacetylacetone with three spectra expands it.



**Figure 3.**  $^1\text{H-NMR}$  spectrum of complex prepared from hexafluoroacetylacetonate as a ligand and nickel as a metal.



**Figure 4.**  $^1\text{H-NMR}$  spectrum of pyrazole (Clark, 2010)

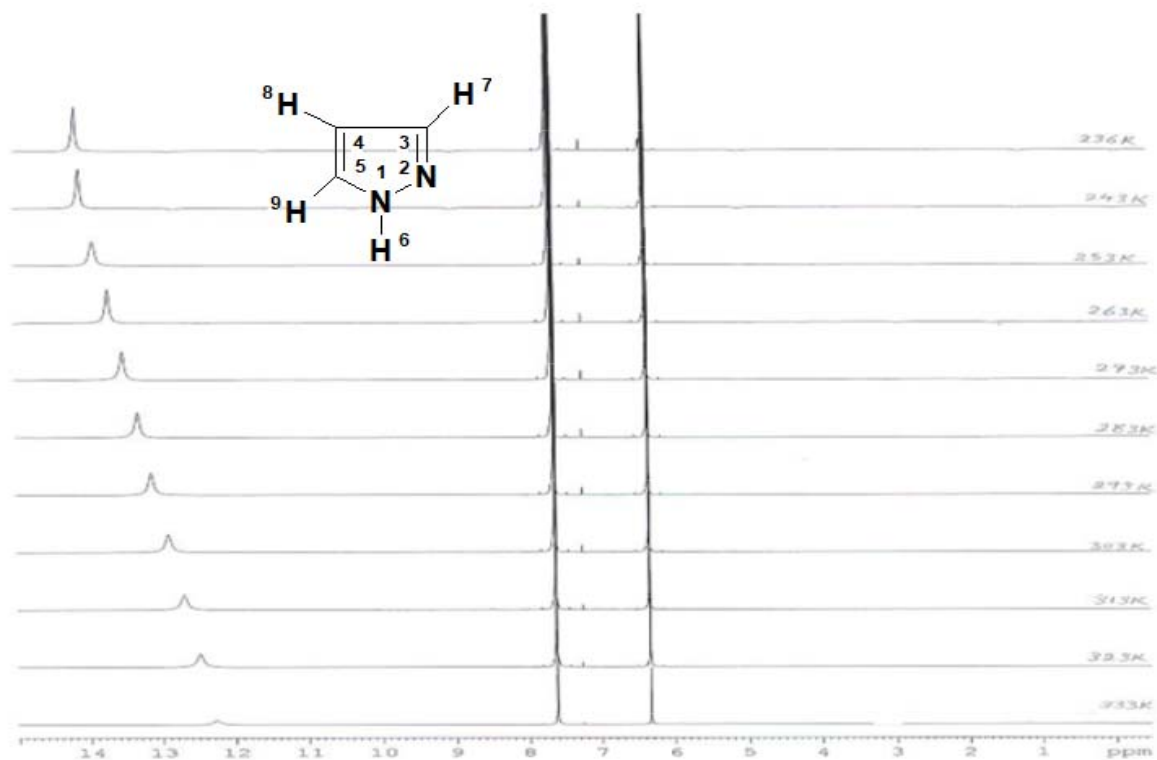


Figure 5. DNMR spectrum of pyrazole (Clark, 2010)

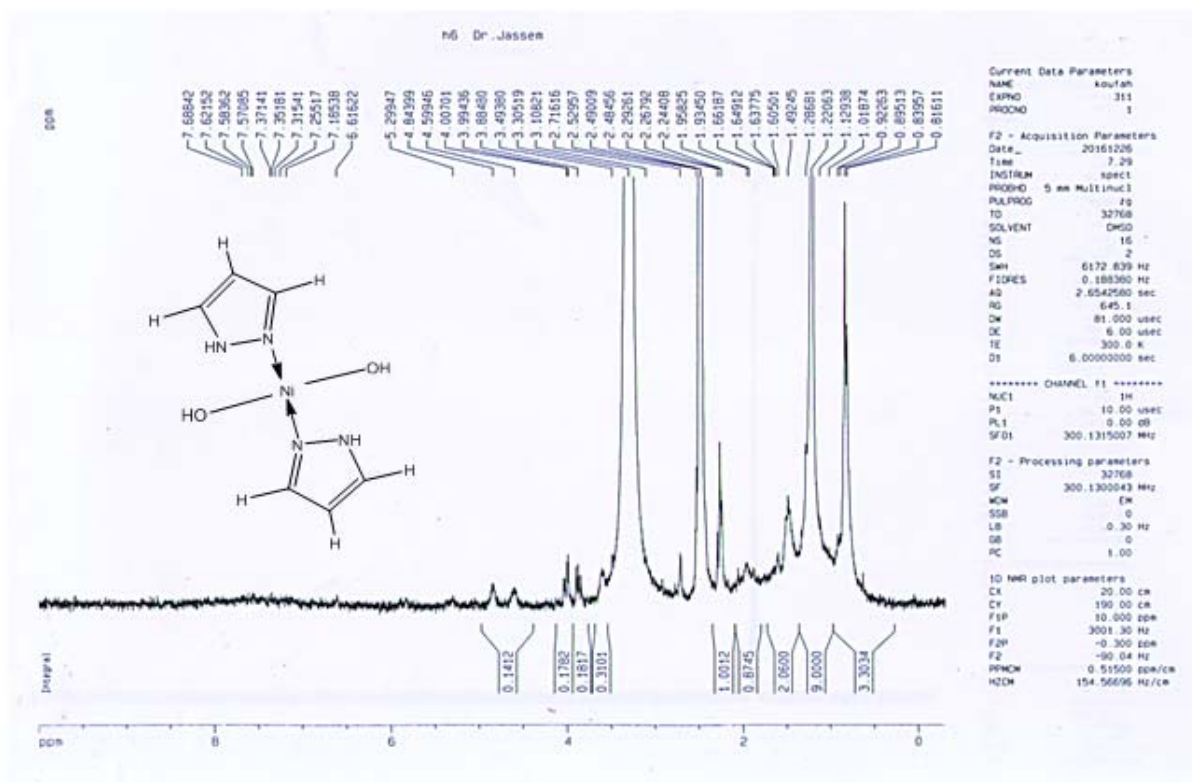
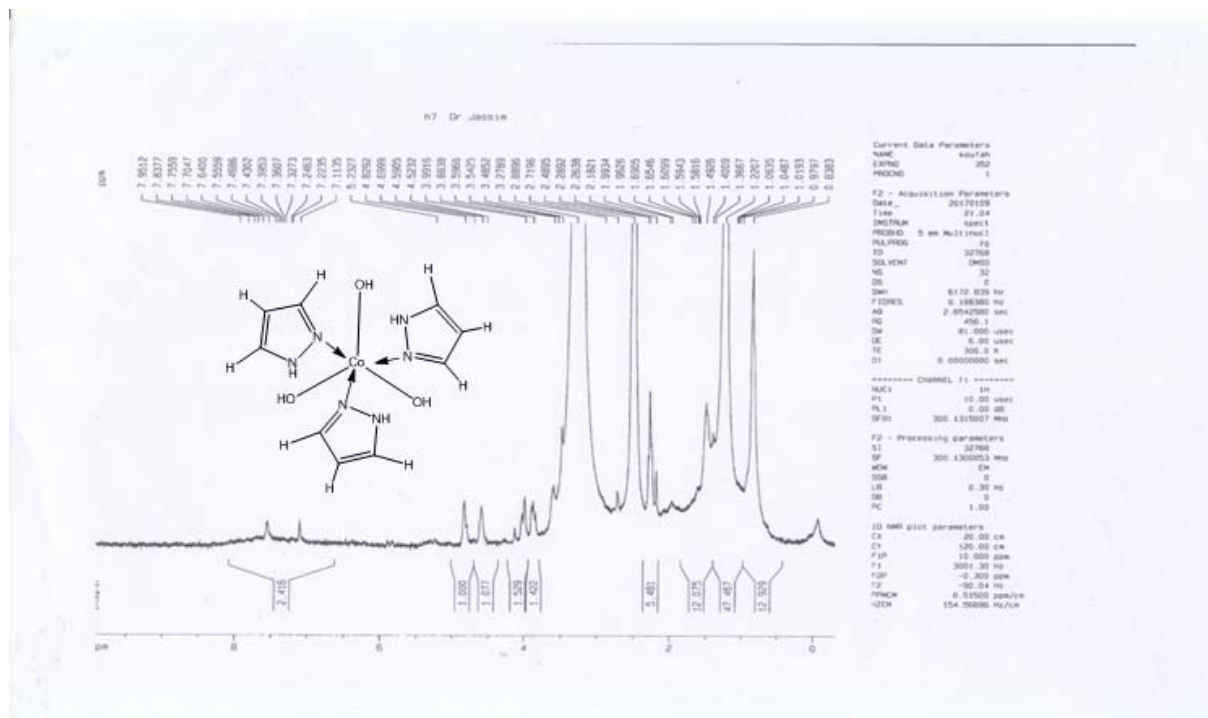
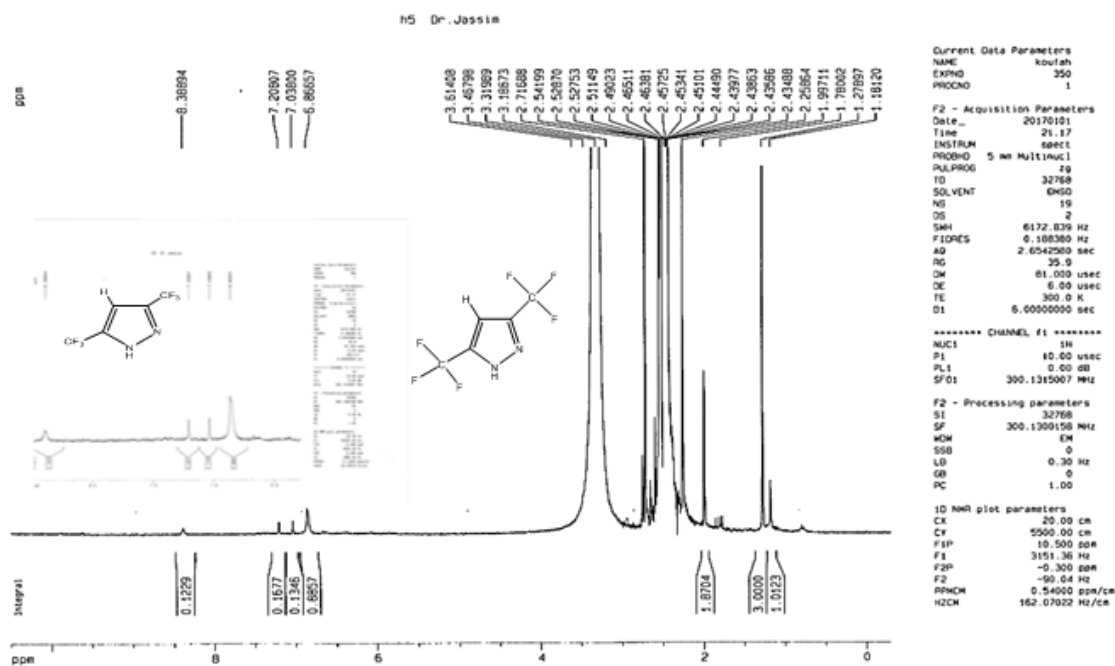


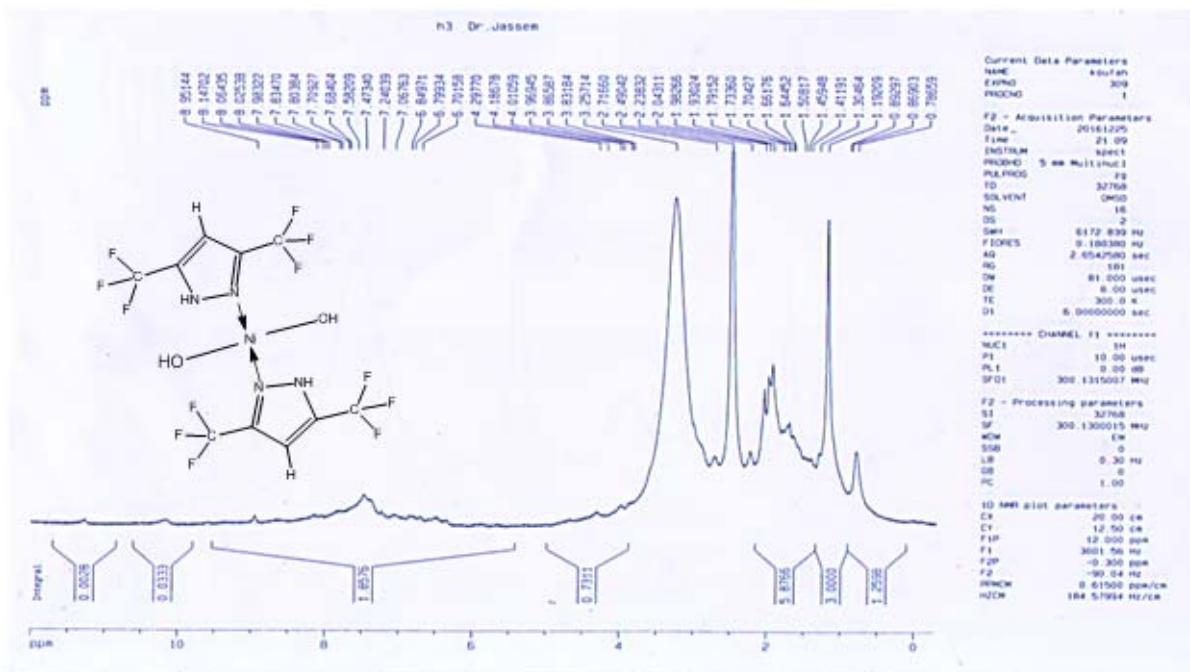
Figure 6. <sup>1</sup>H-NMR spectrum of complex prepared from pyrazole as a ligand and nickel as a metal.



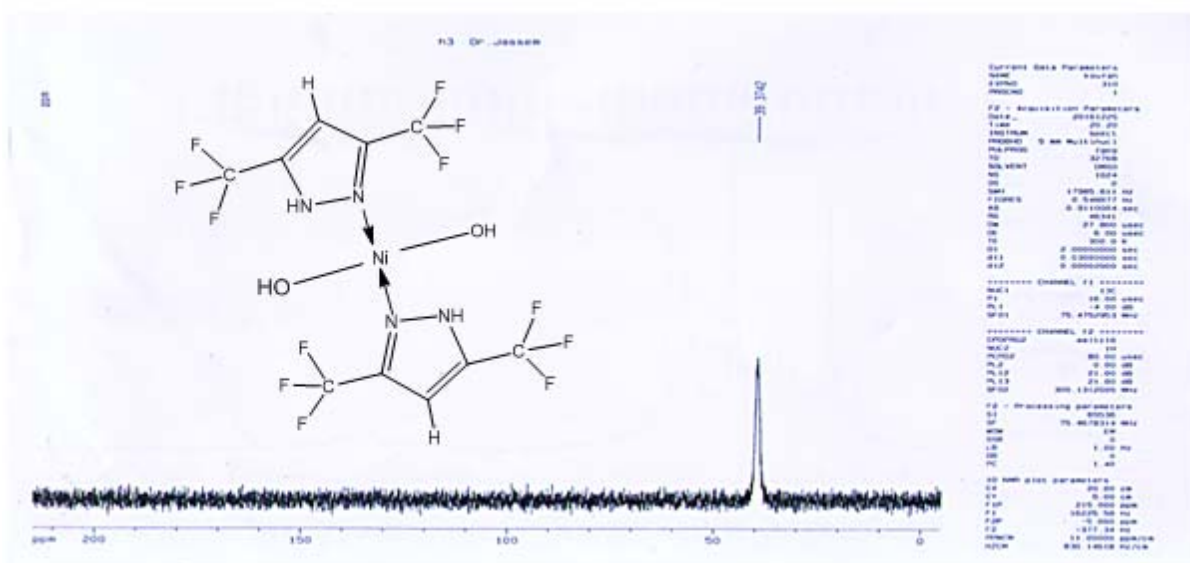
**Figure 7.**  $^1\text{H}$ -NMR spectrum of complex prepared from pyrazole as a ligand and cobalt as a metal.



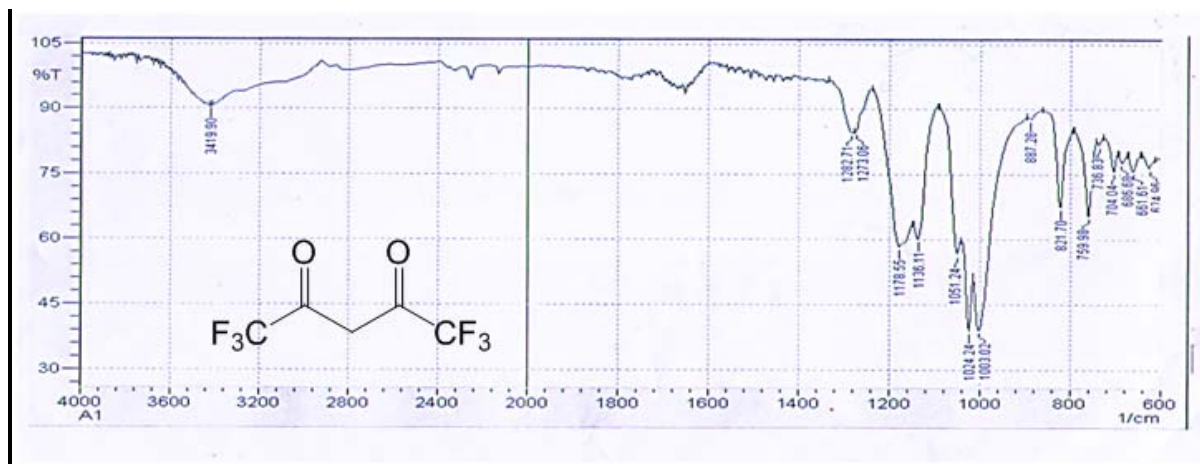
**Figure 8.**  $^1\text{H}$ -NMR spectrum of 3,5-bis(trifluoromethyl)-1H-pyrazole with expansion region at 6.5-8.5 ppm.



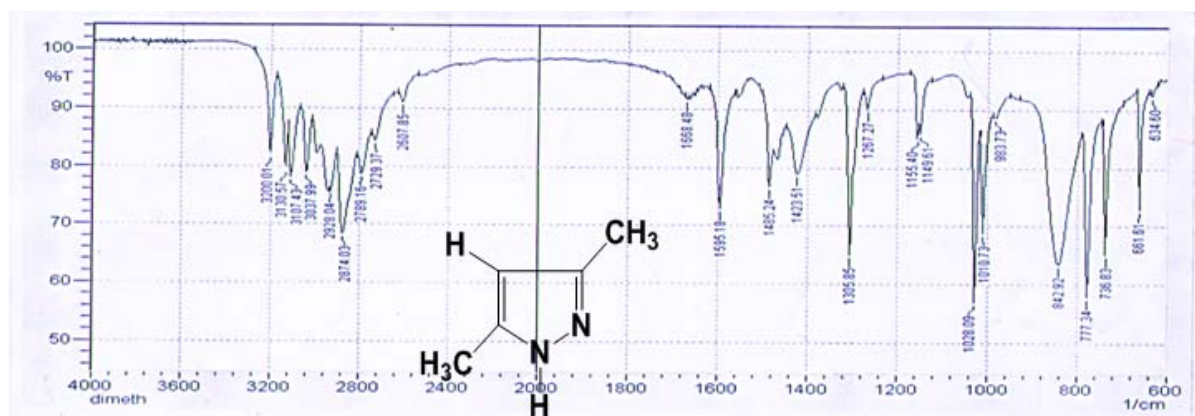
**Figure 9.**  $^1\text{H}$ -NMR spectrum of complex prepared from 3,5 bis(trifluoromethyl)-1H-pyrazole as a ligand and nickel as a metal.



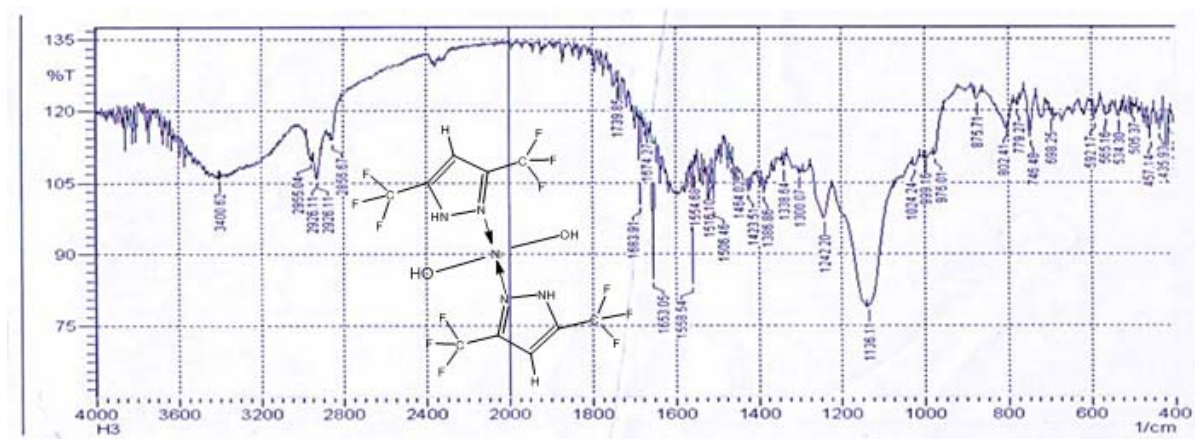
**Figure 10.**  $^{13}\text{C}$ -NMR spectrum of complex prepared from 3,5-bis(trifluoromethyl)-1H-pyrazole as a ligand and nickel as a metal.



**Figure 11.** The FT-IR spectrum of hexafluoroacetylacetone.



**Figure 12.** The FT-IR spectrum of 3,5-dimethylpyrazole.



**Figure 13.** FT-IR spectrum of complex prepared from 3,5-bis(trifluoromethyl)-1H-pyrazole as a ligand and nickel as a metal.