

# Binuclear Divalent Complexes of Cobalt, Nickel and Copper with N<sub>2</sub>S Ligand Derived from 1,3,4-Thiadiazole-2,5-dithiolate Dipotassium Synthesized via Click Chemistry

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## Abstract

A new ligand containing a N<sub>2</sub>S donor set of atoms has been prepared using Click Chemistry from the reaction of 1,3,4-thiadiazole-2,5-dithiol dipotassium salt with propargyl bromide followed by the addition of the product formed from the reaction of sodium azide and octyl iodide, using Cu(I) as catalyst. The ligand was characterized using FT-IR, UV-Vis, <sup>1</sup>H, <sup>13</sup>C NMR spectroscopies and C, H, N elemental analysis. The corresponding Co(II), Ni(II) and Cu(II) complexes were characterized by FT-IR, UV-Vis spectroscopies as well as conductivity and magnetic susceptibility measurements. These measurements suggest that the geometry around the Co is tetrahedral, while around the Ni and Cu it is distorted octahedral. The solubility's of the ligand and its complexes were measured in different solvents.

**Keywords:** thiadiazole, cobalt, nickel, copper complexes, click chemistry

## 1. Introduction

Five membered aromatic systems containing three hetero atoms at symmetrical positions have been studied due to their interesting physiological properties (Hussain, Sharma, & Amir, 2008), as well as their involvement in the life processes (Salimon et al., 2010). More than 90% of new drugs contain heterocyclic compounds indicating the importance of this class of compound to biological and medicinal chemistry (Dua et al., 2011). Aromatic heterocyclic ligands and their metal complexes play key roles as catalysts, anti-HIV, anti-microbial and  $\beta$ -lactamase inhibitors in biological reactions (Suijkerbuijk et al., 2007; Oliva et al., 2010). In addition, this type of compounds has other applications like anticorrosive agents, photographic materials, agrochemicals and dyes (Kumar et al., 2009). Sharpless and Meldal (2002) improved the regioselectivity of the reactions forming heterocyclic molecules by using Cu(I)-catalyzed reactions of organic azides and terminal alkynes (Click Chemistry). The origin of the Cu(I) catalyst can be a Cu(I) salt (e.g. CuI), or generated by oxidation of a Cu(0) complex or reduction of a Cu(II) complex (Martinelli, 2008).

1,3,4-Thiadiazole can act as a ligand and its complexes have a wide variety applications especially as antifungal and antibacterial agents (Samee & Vajragupta, 2011; Kumar, 2010). The Co complexes have been interesting in our life, being a simple example of these compounds B<sub>12</sub> Vitamin a cobalt complex. A simple of these cobalt compounds is B<sub>12</sub> Vitamin which that use as tablets and injections for treatment the verve damage in human body (Chang, 2010). Copper is found in all living organisms and it is important for the function of several enzymes and proteins involved in energy metabolism. Control of the number and type of coordinating atoms is the key for achieving metal complexes that mimics the coordination sphere and reactivity of metal-containing enzymes (Yorimitsu & Oshima, 2006; Cristina et al., 2009; Creaven et al., 2006). Nickel compounds have been interesting for many reasons, in biological systems, nickel forms complexes with adenosine triphosphate, amino acids, peptides, proteins and deoxyribonucleic acid (Reddy et al., 2012; Air Quality Guidelines, 2000). Nickel complexes with sulfur coordination spheres have attracted considerable interest as model compounds for the active centers of nickel sulfur enzymes (Sellman, 2000). Also several nickel compounds have been interested in energy field (Kopera, 2004), Ni(II) can be used as a counter ion in preparation of epoxides (Gash, 2004).

In this study we have synthesized and characterized a heterocyclic ligand containing both a 1,3,4-thiadiazole ring,

and a 1,2,3-triazole ring substituted by long aliphatic chain residues. In addition, the complexes of this ligand with Co(II), Ni(II) and Cu(II) have been isolated.

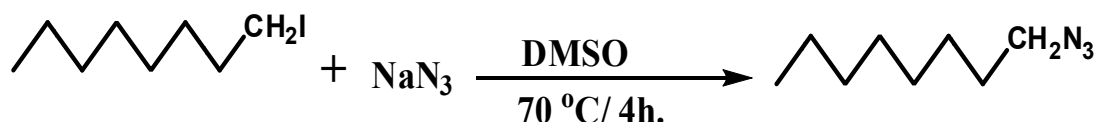
## 2. Experiment

Reagents were purchased from Aldrich, Sigma, Fluka, B. D. H and Qualikems Chemical companies. All chemical have been used without purification, and as supplied by the companies.

IR spectra were recorded as KBr and CsI discs using a Shimadzu 8300 FTIR spectrophotometer in range (4000-400)  $\text{cm}^{-1}$ . Electronic spectra of the prepared compounds were measured in the region (200-1100) nm for 400 ppm solution in DMF at 25 °C using Shimadzu 160 spectrophotometer, with  $1.000 \pm 0.001$  cm matched quartz cell.  $^1\text{H}$ , and  $^{13}\text{C}$ - NMR spectra were acquired with BRUKER-400 spectrometer in DMSO- $d_6$ . The spectra were recorded at Ahl-Albait University, Jordan. C, H, N elemental analysis was performed on a EuroEA elemental analyser (Al-Kufa University). The magnetic susceptibilities were measured on a MSB-Auto Magnetic Susceptibility Balance, (Al-Nahrain University). Electrical conductivity measurements of the complexes were recorded at 25 °C for 400 ppm solution of the sample in DMF using a PW9526 digital conductivity meter.

### 2.1 Preparation of 1-Azido octane

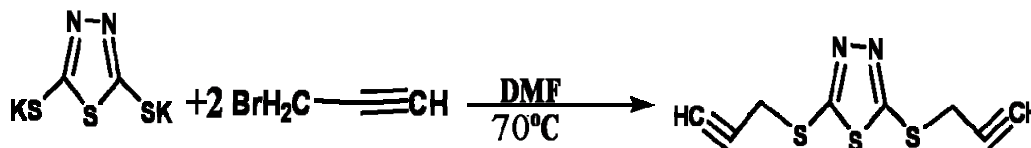
Sodium azide (2.93 g, 45 mmol) was added to a stirred solution of octyl iodide (3.60 g, 15 mmol) in DMSO (50 mL) and the resulting suspension was stirred at 70 °C for 4 h. The reaction mixture was then poured into water (100 mL) and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 50$  mL). The combined ethereal layers were washed with a saturated solution of NaCl (50 mL) then dried over  $\text{Na}_2\text{SO}_4$ . Evaporation under reduced pressure gave 1-azido octane as a colorless liquid (yield = 59.3%).



Scheme 1. Preparation of 1-Azido octane

### 2.2 Preparation of 2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole

Propargyl bromide (2.856 g, 24 mmol) was added to a stirred solution of 1,3,4-Thiadiazole-2,5-dithiol dipotassium salt (2.856 g, 24 mmol) in DMF (40 mL), then heated to 70 °C for 24 h. subsequently, the solution was poured into ice water (80 mL) and extracted with  $\text{Et}_2\text{O}$  ( $3 \times 40$  mL). The combined ethereal layers were washed with a saturated solution of NaCl (50 mL), dried over  $\text{Na}_2\text{SO}_4$  and then evaporated under reduced pressure to give 2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole. Recrystallization from n-hexane gave the product as white needle crystals in 38% yield.

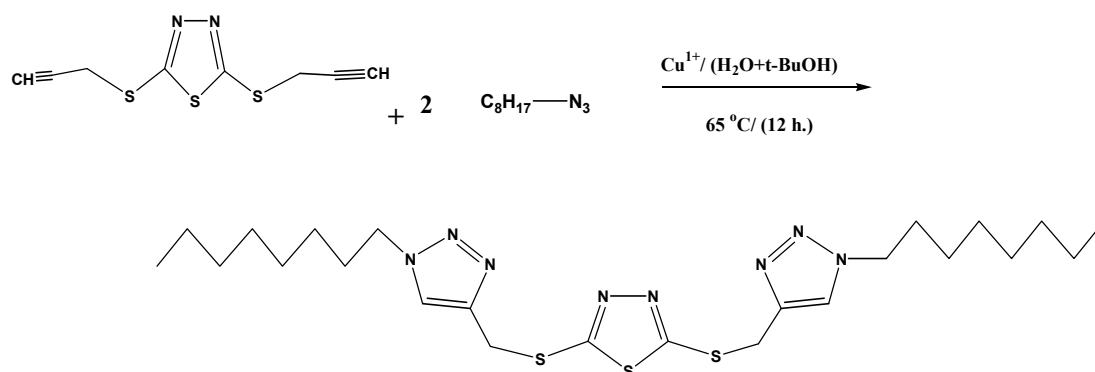


Scheme 2. Preparation of 2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole

### 2.3 Preparation of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole

2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole (0.226 g, 1.0 mmol.) was dissolved in dichloromethane (9 mL), and then mixed with copper sulfate (0.0250 g, 0.1 mmol) and sodium-L-ascorbate (0.0396 g, 0.2 mmol) dissolved in distilled water with t-butane (water: butanol = 2:1). 1-Azido octane (0.388 g, 2.5 mmol.) was now added and the mixture was stirred at 65 °C for 12 h. to form a, white precipitate. This solid was, dissolved in dichloromethane (10 mL), then dried over  $\text{Na}_2\text{SO}_4$ . Purification was achieved by eluting the solution down a column of silica gel (mesh 60). Evaporation of the product under reduced pressure gave 2,5-bis[(1-octyl-1H-1,2,3-triazol-4-yl)

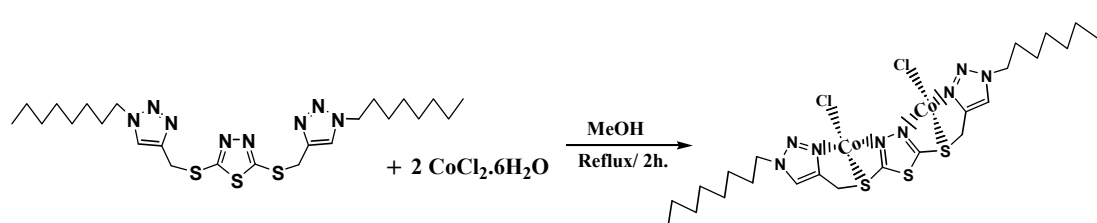
methylthio]-1,3,4-thiadiazole in 83% yield.



Scheme 3. Preparation of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole

#### 2.4 Preparation of Cobalt(II) Complex

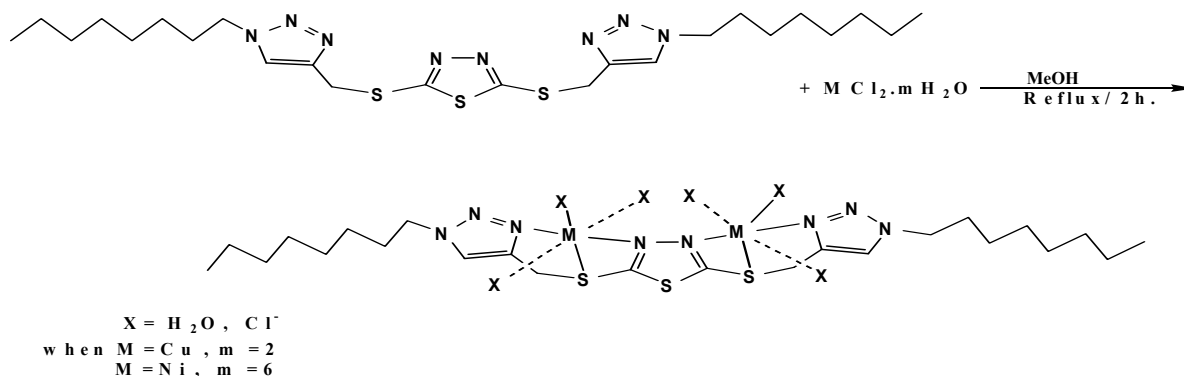
Cobalt chloride.  $6\text{H}_2\text{O}$  (0.0188 g, 0.1117 mmol) was dissolved in MeOH (5 mL), then added to a solution of the ligand (0.03 g, 0.0558 mmol) dissolved in MeOH. The solution was refluxed for 2 h. to produce a blue precipitate. The solid was removed by filtration, washed with  $\text{Et}_2\text{O}$  (5 mL) and cold MeOH (5 mL). The solid was recrystallized from acetonitrile.



Scheme 4. Preparation of Cobalt(II) complex

#### 2.5 Preparation of Nickel(II) Complex

Nickel chloride  $6\text{H}_2\text{O}$  (0.0188 g, 0.1117 mmol) was dissolved in MeOH (5mL), then added to a solution of the ligand (0.03 g, 0.0558 mmol) dissolved in MeOH (5 mL). The mixture was refluxed for 2 h. producing a yellow-green precipitate which was removed by filtration. The solid was washed with  $\text{Et}_2\text{O}$  (5 mL) and cold MeOH (5 mL) then recrystallized from acetonitrile.



Scheme (5) Preparation of Nickel & Copper (II) complexes

### 2.6 Preparation of Copper(II) Complex

Copper chloride  $2\text{H}_2\text{O}$  (0.0178 g, 0.1117 mmol) was dissolved in MeOH (5 mL), then added to a solution of ligand (0.03 g, 0.0558 mmol) dissolved in MeOH (5 mL). The mixture was refluxed for 2 h producing a green-yellow precipitate. The solid was removed by filtration then, washed with  $\text{Et}_2\text{O}$  (5 mL) and cold MeOH (5 mL). The complex was recrystallized from acetonitrile.

### 3. Results and Discussion

The ligand was prepared from two precursors: compound 1 (synthesized from the reaction of the sodium azide with octyl iodide) and compound 2 (obtained from the reaction of propargyl bromide with 1,3,4-thiadiazole-2,5-dithiol dipotassium salt), using Click Chemistry catalyzed by Cu(I). This ligand reacts with Co(II), Ni(II) and Cu(II) salts to produce binuclear complexes. The solubility of all compounds was determined in different solvents Table 1.

Table 1. Solubility of ligand and complexes

Compound	DCM	$\text{CH}_3\text{CN}$	$\text{Et}_2\text{O}$	Acetone	$\text{C}_6\text{H}_{14}$	MeOH	$\text{CHCl}_3$	$\text{H}_2\text{O}$	t-BuOH	DMSO	DMF
Ligand	+	+	-	÷	-	+	+	-	-	+	+
$[\text{Co}_2\text{C}_8\text{L mH}_2\text{OxCl}]$	+	+	-	+	-	+	+	-		+	+
$[\text{Ni}_2\text{C}_8\text{L mH}_2\text{OxCl}]$	-	-	-	÷	-	-	-	-	-	+	+
$[\text{Cu}_2\text{C}_8\text{L mH}_2\text{OxCl}]$	+	+	-	+	-	+	+	-	-	+	+

(+) Soluble    (-) Insoluble    (÷) Sparingly soluble

#### 3.1 Elemental Analysis

The C, H, N elemental analysis of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole is in good agreement with the theoretical values. Table 2 shows the theoretical and calculated percentage of C, H, N and S elements. The theoretical data was calculated using the Chem Office, CS ChemDraw Ultra program by drawing the molecules and use the analyze structure.

Table 2. Melting point and C.H.N elemental analysis of ligand

Compound	Empirical Formula	M.W	Yield%	m.p <sup>0</sup> C	Colour	Found, (calc) %			
						C	H	N	S
Ligand	$\text{C}_{24}\text{H}_{40}\text{N}_8\text{S}_3$	536.82	85.44	109.5°C	Off	53.326	7.366	20.474	17.808
					white	(53.70)	(7.51)	(20.87)	(17.92)

Calculated values shown in parentheses.

#### 3.2 FT-IR Spectra Data of the Precursors, Ligands and Complexes

The IR spectrum of 1-azido-octane Figure 1 exhibits bands at  $\nu = 2956\text{--}2927\text{ cm}^{-1}$  assigned to symmetrical and asymmetrical stretches of aliphatic (C-H). The strong band at  $\nu = 2096\text{ cm}^{-1}$  is attributed to the stretching of  $\text{N}_3$ . The bands at  $\nu = 1259\text{ cm}^{-1}$  and  $\nu = 1124\text{ cm}^{-1}$  are assigned to stretching of C-N and C-C respectively (Silverstein, 1998). The IR spectrum of 2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole Figure 2 displays band at  $\nu = 3210\text{ cm}^{-1}$  due to stretching of (C-H bond in terminal alkynes). While the band at  $\nu = 2111\text{ cm}^{-1}$  is characteristic of ( $\text{C}\equiv\text{C}$  stretching). The bands at  $\nu = 1396\text{--}1375\text{ cm}^{-1}$  can be attributed to bending of aliphatic (C-H). The bands at  $\nu = 1058\text{ cm}^{-1}$ ,  $952\text{ cm}^{-1}$  and  $865\text{ cm}^{-1}$  are attributed to the (N-N) and (C-H) groups in the plane of the alkynes and out of the plane respectively. The band at  $\nu = 698\text{ cm}^{-1}$  is assigned to the C-S bond of thiadiazole (Silverstein, 1998). The IR spectrum of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole Figure 3 shows a band at  $\nu = 1548\text{ cm}^{-1}$  assigned to stretching of the C=N bond of the triazole ring,. The bands at  $\nu = 1386\text{ cm}^{-1}$ ,  $1238\text{ cm}^{-1}$  and  $1058\text{ cm}^{-1}$  are due to stretching of N=N, C-N, and

N-N (tri-azole ring) respectively (Silverstein, 1998).

The IR spectrum of the Co(II) complex Figure 4 shows bands at  $\nu = 3441\text{ cm}^{-1}$  and  $3132\text{ cm}^{-1}$  referred to O-H stretching of water molecules and (C-H of the aromatic ring in triazole. The bands at  $\nu = 1552\text{ cm}^{-1}$ ,  $1465\text{ cm}^{-1}$  and  $1382\text{ cm}^{-1}$  are assigned to stretching of (C=N, C=C and (N=N respectively, whilst the bands at  $\nu = 1224\text{ cm}^{-1}$  and  $1047\text{ cm}^{-1}$  assigned to C-N and N-N were shifted about 14 to 11  $\text{cm}^{-1}$  compared to the value of the uncoordinated molecule. This indicates that the N atom is coordinated to cobalt. In addition, the new bands at  $\nu = 584\text{ cm}^{-1}$  and  $495\text{ cm}^{-1}$  (assigned to M-N and (M-S respectively) indicate that coordination of the ligand and cobalt has taken place (Silverstein, 1998; Nakamoto, 1996).

The IR spectrum of the Ni(II) complex Figure 5 shows bands at  $\nu = 3381\text{ cm}^{-1}$  and  $3131\text{ cm}^{-1}$  are assigned to O-H stretching water molecules and (C-H stretches of the aromatic triazole ring. The bands at  $\nu = 1552\text{ cm}^{-1}$ ,  $1465\text{ cm}^{-1}$  and  $1381\text{ cm}^{-1}$  are assigned to stretching of C=N, C=C and N=N respectively. The bands at  $\nu = 1226\text{ cm}^{-1}$  and  $1056\text{ cm}^{-1}$  assigned to C-N and N-N stretches respectively (Silverstein, 1998; Nakamoto, 1996) are shifted about 10 to 20  $\text{cm}^{-1}$  compared to the uncoordinated molecule.

The IR spectrum of the Cu(II) complex Figure 6 shows band at  $\nu = 3444\text{ cm}^{-1}$  and  $3132\text{ cm}^{-1}$  assigned to O-H stretches of water molecules and C-H of the aromatic triazole ring., The bands at  $\nu = 1556\text{ cm}^{-1}$ ,  $1456\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  are assigned to stretches of C=N, C=C and N=N respectively. The bands at  $\nu = 1246\text{ cm}^{-1}$  and  $1049\text{ cm}^{-1}$  (assigned to C-N and N-N stretches) are shifted about 10 to 15  $\text{cm}^{-1}$  compared to the uncoordinated molecule (Silverstein, 1998; Nakamoto, 1996).

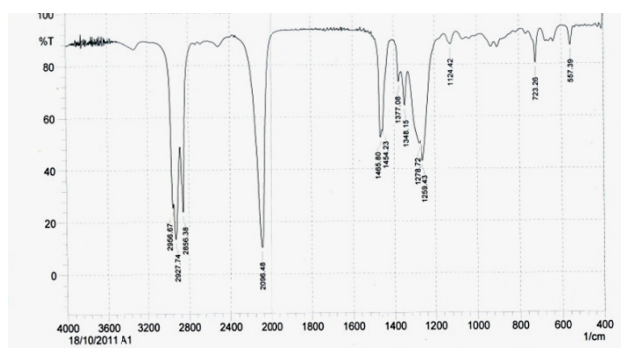


Figure 1. I spectrum of 1-Azido octane

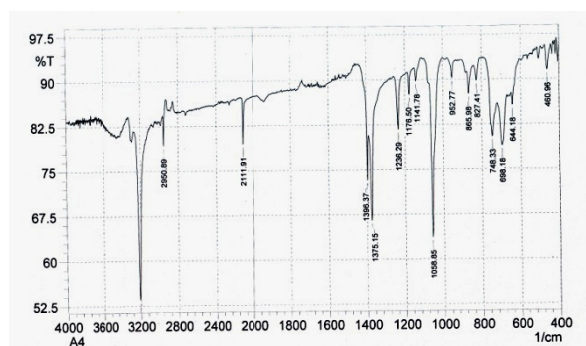


Figure 2. IR spectrum of 2,5-bis(prop-2-ynylthio)-1,3,4-thiadiazole

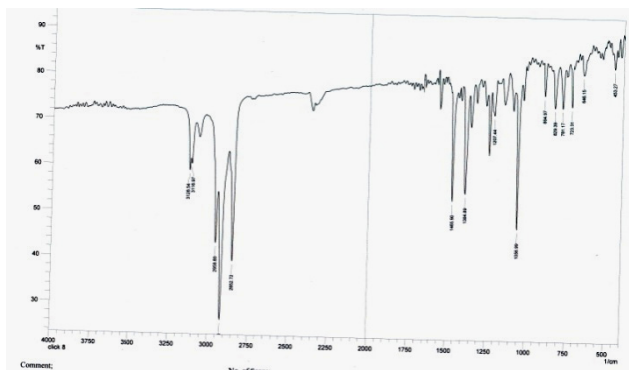


Figure 3. IR spectrum of the ligand

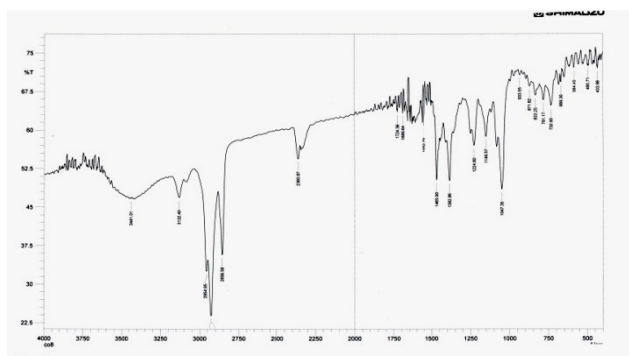


Figure 4. IR spectrum of cobalt(II) complex

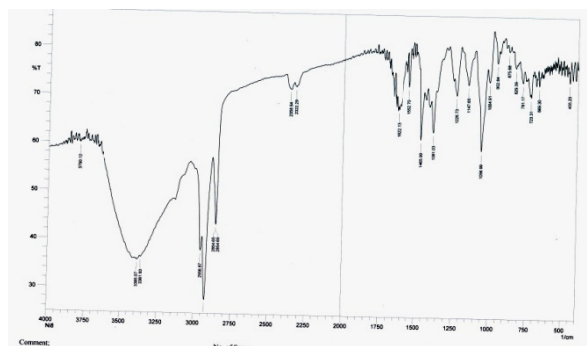


Figure 5. IR spectrum of Nickel(II) complex

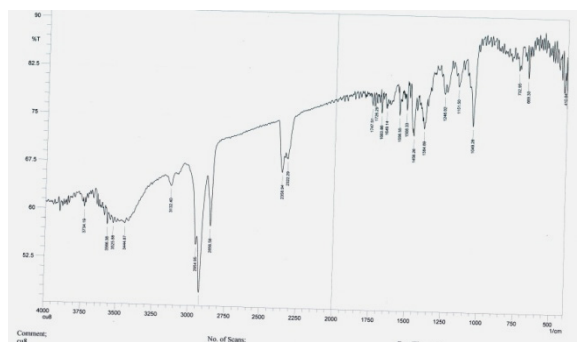


Figure 6. IR spectrum of copper(II) complex

### 3.3 $^1\text{H}$ NMR Spectrum of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole

$^1\text{H}$  NMR spectrum of the ligand Figure 7 (in DMSO- $d_6$ ) consists of a peak at  $\delta = 0.836$  ppm, 6H is assigned to terminal ( $-\text{CH}_3$ ) in aliphatic octyl chain. The peaks at  $\delta = 1.213$ – $1.761$  ppm, (14H) are due to the  $-\text{CH}_2-$  groups in the aliphatic chain, while the signal at  $\delta = 3.336$  ppm, (4H) are assigned to protons of the aliphatic chain attached to N atom in triazole ring. The peaks at  $\delta = 4.355$  and  $4.550$  ppm, (4H) are assigned to the protons  $\text{CH}_2$  group attached to sulfur atom and triazole ring refer to the protons have a different environments, signal at ( $\delta = 8.067$  ppm, 2H) attributed to protons of aromatic triazole ring (Silverstein, 1998).

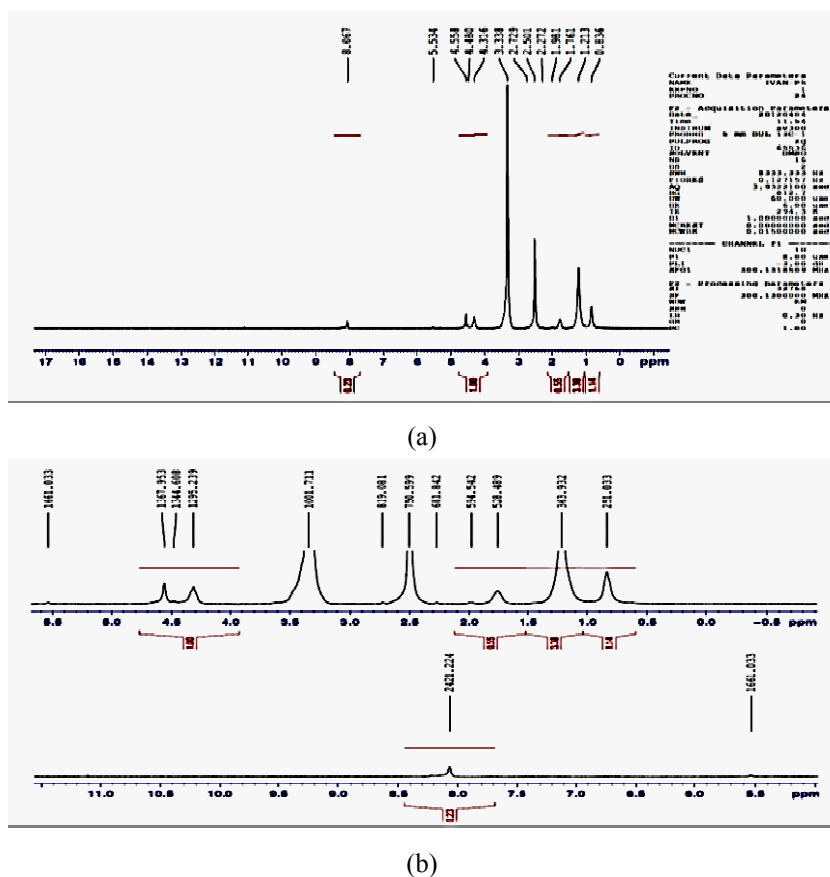
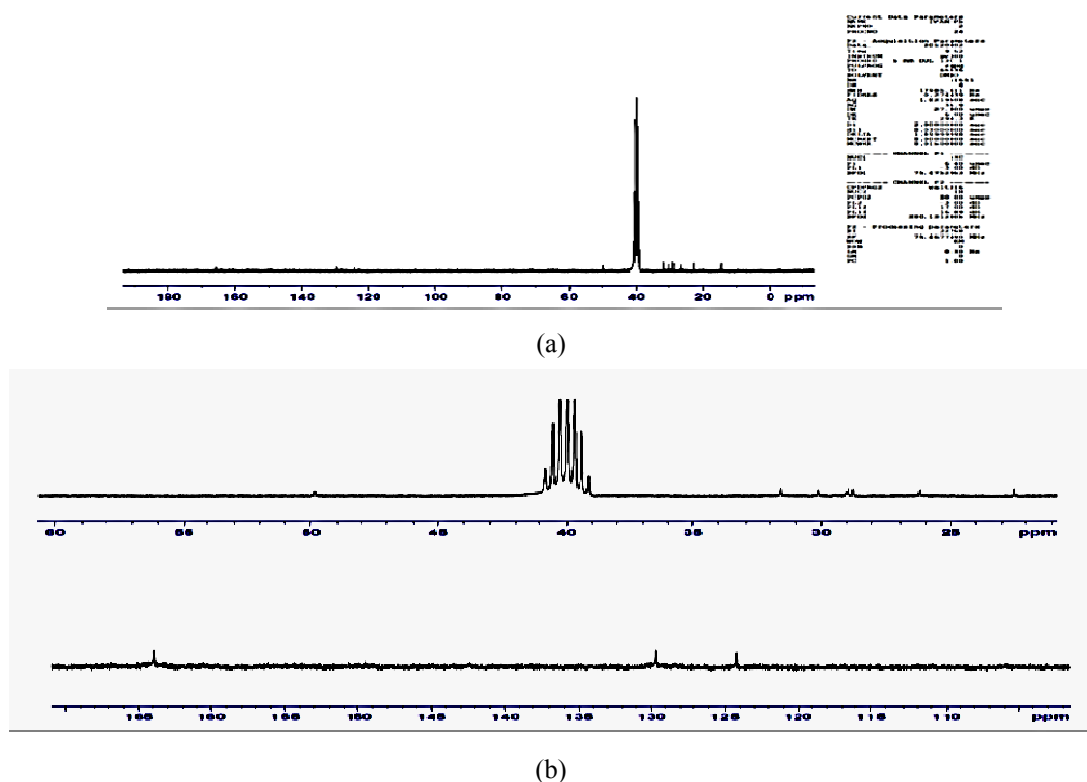


Figure 7.  $^1\text{H}$ NMR spectrum of the Ligand

### 3.4 $^{13}\text{C}$ NMR Spectrum of 2,5-bis[1-octyl-1H-1,2,3-triazol-4-yl] methylthio]-1,3,4-thiadiazole

The  $^{13}\text{C}$  NMR spectrum of the ligand Figure 8 displays a signal at  $\delta = 14.12$  ppm attributed to the terminal methyl group of the octyl residue. Signals between ( $\delta = 22.32$ – $33.35$  ppm) are assigned to the aliphatic chain carbon atoms, while the carbon atom which attached to N of the triazole ring appears at ( $\delta = 49.88$  ppm). The carbon atoms of the triazole ring show two signals at  $\delta = 124.12$  and  $129.89$  ppm., The peaks at  $\delta = 164.1$  are assigned to the carbon atoms in the thiadiazole ring (Silverstein, 1998).

Figure 8.  $^{13}\text{C}$  HNMR spectrum of the Ligand

### 3.5 UV-Vis Spectra of Ligand and Complexes

The electronic spectra of the ligand and their complexes are shown in Figures 9 to 12. The spectrum of the ligand displays broad peaks at  $\lambda = 231$  and  $293$  nm attributed to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$ . The UV-Vis spectrum of the cobalt(II) complex shows a broad peak at  $\lambda = 250$ – $310$  nm due to the ligand field and charge transfer. The visible region contains peaks at  $\lambda = 637$ ,  $610$  and  $572$  nm due to the d-d transition  $^4\text{A}_2 \rightarrow ^4\text{T}_2$ ,  $^4\text{A}_2 \rightarrow ^4\text{T}_1$ ,  $^4\text{A}_2 \rightarrow ^4\text{T}_1^{(p)}$  respectively which suggests a tetrahedral geometry around the cobalt. The UV-visible spectrum of the nickel(II) complex exhibits peaks in the visible region at  $\lambda = 588$ ,  $564$ ,  $410$  nm due to  $^3\text{A}_2 \rightarrow ^3\text{T}_2$ ,  $^3\text{A}_2 \rightarrow ^3\text{T}_1$ ,  $^3\text{A}_2 \rightarrow ^3\text{T}_1^{(p)}$ . The UV-visible spectrum of the copper(II) complex displays a broad peak in the UV region due to ligand field and charge transfer bands. The d-d transitions appear in the visible region at  $\lambda = 735$  nm attributed to the transition type  $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$ , corresponding to an octahedral geometry around the copper (Nakamoto, 1996).

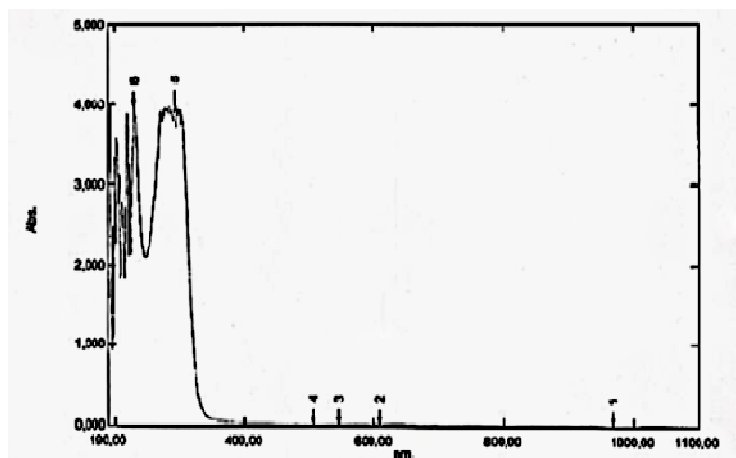


Figure 9. UV-Vis spectrum of Ligand



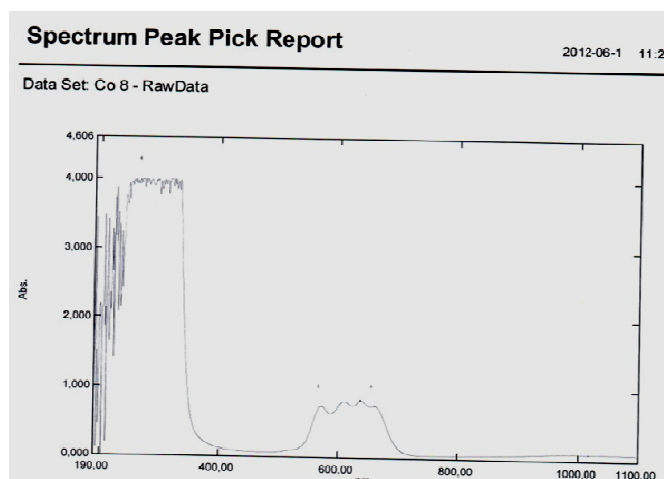


Figure 10. UV-Vis spectrum of Cobalt (II) complex

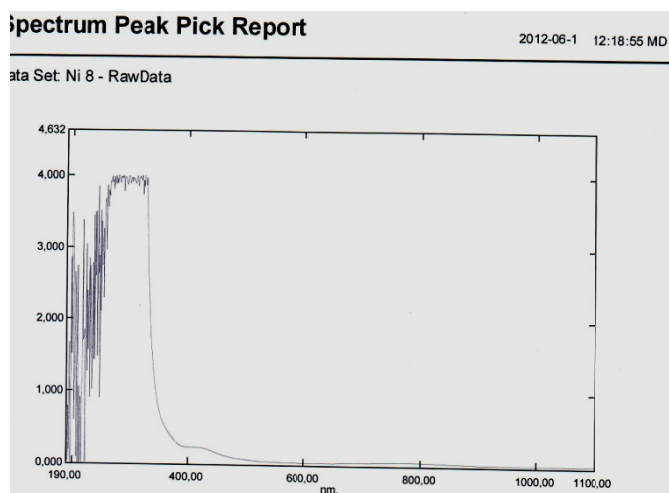


Figure 11. UV-Vis spectrum of Nickel (II) complex

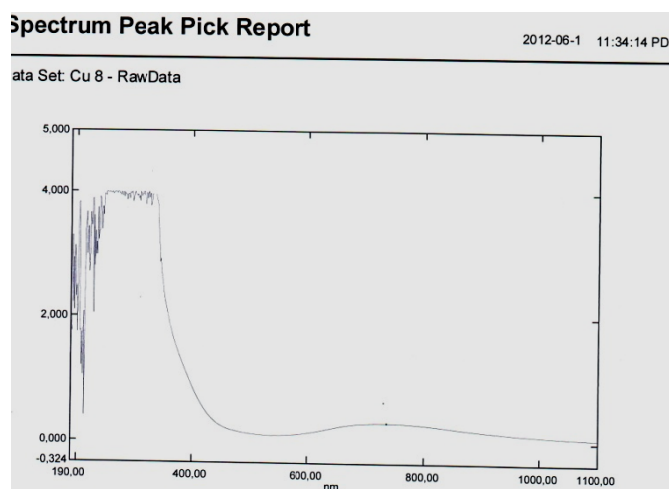


Figure 12. UV-Vis spectrum of Copper (II) complex

### 3.6 Conductivity Measurements of Complexes

The molar conductivity of the complexes in DMF solution shows that the cobalt and nickel complexes are 1:2 electrolytes, while the copper complex is a 1:4 electrolyte.

### 3.7 Magnetic Moments of Complexes

The magnetic moments of the complexes were calculated from the measured magnetic susceptibilities. All the complexes were paramagnetic as shown by the results presented in Table 3. The magnetic moments was calculated from the magnetic susceptibility by treatments the gram magnetic susceptibility into the molar magnetic susceptibility then multiply by Paschal constant for elements and metals. From the results we observed the lower value than the calculated due to the some coupling taken place.

Table 3. Physical properties of synthesis complexes

No.	Complex	M.p.	Color	Magnetic Moments B.M.	Conductivity $\mu\text{Sem.cm}^{-1}$	Suggested geometry
1.	$[\text{Co}_2\text{C}_8\text{L Cl}_2]\text{Cl}_2$	192°C	Blue	4.45	1.82	$T_d$
2.	$[\text{Ni}_2\text{C}_8\text{L} \cdot 2\text{H}_2\text{O} \cdot \text{Cl}_2]\text{Cl}_2$	235°C Dec.	Yellowish-green	2.88	2.72	$O_h$
3.	$[\text{Cu}_2\text{C}_8\text{L}4\text{H}_2\text{O}]\text{Cl}_4$	107°C	Greenish-yellow	1.81	4.5	$O_h$

Dec.: decomposed,

B.M.: Bohr magneton

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