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# Synthesis and Characterization of *Hexathiosianatoiron(II)* [Fe(NCS)$_6$]$^{4-}$ Complex Compound and *Tetrapyridindithiosianatoiron(II)* [Fe(NCS)$_2$(Py)$_4$] Complex Compound

Fitria Febrianti[1*], Ani Sutiani[1], Iis Siti Jahro[1], Asep Wahyu Nugraha[1], and Nabila Nur Fadhila[2].

[1]*Department of Chemistry, Faculty of Mathematics and Sciences, Universitas Negeri Medan, Medan 20221, Indonesia*
[2]*Department of Chemistry, Faculty of Mathematics and Sciences, Institut Teknologi Bandung, Ganesha 10 Badung 40132, Indonesia*
[*]*Corresponding author: fitrrrrria@gmail.com*

## ABSTRACT

*This research aims to synthesize and characterize the complex compounds Hexathiocyanatoiron(II) [Fe(NCS)$_6$]$^{4-}$ and Tetrapyridinedithiocyanatoiron(II) [Fe(NCS)$_2$(Py)$_4$]. The synthesis of these complex compounds was conducted in the Chemistry Laboratory, Faculty of Mathematics and Natural Sciences, Medan State University, while magnetic susceptibility measurements were carried out using the Magnetic Susceptibility Balance (MSB) instrument in the Inorganic Chemistry Laboratory, Bandung Institute of Technology. The complex compound synthesis involved the reaction of Iron(II) sulfate heptahydrate with Potassium thiocyanate and Pyridine compound in a 1:2 and 1:2:4 molar ratio. The synthesis process was conducted through a direct reaction method in a polar solvent. The obtained results include Hexathiocyanatoiron(II) complex compound, [Fe(NCS)$_6$]$^{4-}$, which is pale yellow crystalline with a yield of 32.76%, and Tetrapyridinedithiocyanatoiron(II) complex compound, [Fe(NCS)$_2$(Py)$_4$] which is dark purple crystalline with a yield of 52.62%. These compounds exhibit a melting point of 219°C. Magnetic susceptibility measurements using the MSB instrument revealed a magnetic susceptibility of 6.69 BM (paramagnetic) for the Hexathiocyanatoiron(II) complex[Fe(NCS)$_6$]$^{4-}$, and a magnetic moment of 5.61 BM (diamagnetic) for the Tetrapyridinedithiocyanatoiron(II ) complex [Fe(NCS)$_2$(Py)$_4$].*

*Keywords: Iron, ligand effect, magnetic properties, magnetic moment value, Magnetic Susceptibility Balance*

## 1. INTRODUCTION

Metal complexes exhibit diverse and intriguing characteristics that warrant investigation. These complex compounds find numerous applications in various fields such as catalysis, electroplating[1], pharmaceuticals[2], sacred materials or sensors, and data storage materials[3]. In complex compounds, the metal component is typically derived from transition metals. Iron(II) ions, a transition metal, possess four unpaired electrons, with partially filled *d* orbitals, leading to variations in their chemical and physical properties. In this context, the addition of ligands introduces differences in magnetic properties, resulting in diamagnetic behavior in the low-spin (LS) state with an electron configuration of $t_{2g}^6 e_g^0$ when strong ligands are involved and paramagnetic behavior in the high-spin (HS) state with an electron configuration of $t_{2g}^4 e_g^2$ when weak ligands are present[5-6].

In octahedral transition metal ions with electron configurations ranging from $3d^4$-$3d^7$, the electron filling leads to partial orbital degeneracy in the *3d* orbitals, specifically in $t_{2g}$ and $e_g$ energy levels. The electron filling in $t_{2g}$ and $e_g$ orbitals depends on the ligand field strength and the energy required to pair two electrons in the same orbital. Strong ligand fields result in a significant energy gap, which encourages electron pairing in the $t_{2g}$ orbitals, yielding the maximum number of paired electrons and inducing a low-spin state. Conversely, weak ligand fields result in a lower energy gap and a maximum number of unpaired electrons, leading to a high-spin state, as filling the $e_g$ set requires less energy than pairing electrons in the $t_{2g}$ set[7].

Most ligands used in the formation of complex compounds are organic compounds. This is because they are easier to experimentally form and modify compared to inorganic compounds[8]. In theory, a ligand's ability to fill *d* orbitals in complex compounds of iron(II) metal ions will result in partial degeneracy of orbitals, leading to energy levels in the $t_{2g}$ and $e_g$ orbitals, the filling of these two orbitals is influenced by the ligand field strength and the energy required to pair two electrons in the same orbital[9], the results of this filling provide information about the magnetic properties of the synthesis process.

Ligands like thiocyanate and pyridine have been widely employed in the synthesis of complex compounds, and the properties of these compounds, such as their magnetic behavior, have been extensively studied through reaction stages involving different metal ions and ligands. The synthesis of dithiocyanatotetrapyridineiron(II) compounds has been carried out in two isomeric forms, namely *α*-Fepy$_4$(NCS)$_2$ and *β*-Fepy$_4$(NCS)$_2$,  with both crystals exhibiting crystal magnetic moments of 5.38 BM and 5.52 BM respectively[10]. In other cases, the synthesis of Fe(II) thiocyanate complex compounds using pyridine derivative ligands has shown that successfully synthesized compounds exhibit a high spin state in an octahedral configuration[11].

In another context, in line with the advancement of technology, research into determining the magnetic properties and magnetic moment values of complex compounds has been conducted using computational methods, particularly Density Functional Theory (DFT), referring to the work by Kaneko M. & Nakashima S. (2015), it is explained that the use of DFT is focused on elucidating the phenomenon of spin crossover (SCO) in Fe(II) metal, which involves changes in magnetic properties between the high-spin (hs) and low-spin (ls) states. DFT is focused on geometry optimization with constraints on the bond interactions between the metal and ligand in trans Fe(NCS)$_2$(py)$_4$ complex compounds by improving the dihedral angle between Fe and NCS and the geometry of pyridine, the results indicate an energy difference between the high-spin (hs) and low-spin (ls) states, which is obtained from the analysis of orbital *d* overlap and Fe atom energy separation due to ligand

field correction, this identifies a correlation between the ls state and the change in the SCO ground state energy ($\Delta E_0$), Identifying the ground state LS depends on the fundamental SCO (spin-crossover) changes[12].

The influence of ligands in the synthesis of complex compounds is intriguing and warrants investigation. The choice of ligand type has a varying impact on each metal ion in complex compounds. In this study, the results of the synthesis and characterization of iron(II) complex compounds using two different monodentate ligands with distinct ligand field properties are described. The use of different ligands with varying ligand field properties is employed to determine the effects of ligand type on the magnetic properties of iron(II) complex compounds.

## 2. EXPERIMENTAL

### 2.1. Chemicals, Equipment and Instrumentation

The required chemical materials include Iron(II) sulfate heptahydrate ($FeSO_4.7H_2O$) (*Merck*), potassium thiocyanate (KSCN), pyridine ($C_5H_5N$) (*Merck*), nitrogen gas, methanol ($CH_3OH$), and distilled water. The necessary equipment comprises Erlenmeyer flasks, pipettes, graduated cylinders, analytical balances, stirring rods, thermometers, hot plates, magnetic stirrers, desiccators, spatulas, watch glasses, glass funnels, ovens, filter papers, and aluminum foil. The instruments utilized in this research are the magnetic susceptibility balance (MSB) and the melting point apparatus.

### 2.2. Research Procedure

**Synthesis [complex 1] compounds hexa-thiocyanate-iron(II) $[Fe(NCS)_6]^{4-}$**: In 10 mL of methanol, 0.278 g of $FeSO_4.7H_2O$ was dissolved and stirred using a magnetic stirrer while being purged with nitrogen gas. Subsequently, 0.194 g of KSCN was weighed and dissolved in 10 mL of methanol. Next, the KSCN solution was added dropwise to the iron(II) solution. The precipitate formed was filtered, washed with methanol and distilled water, and then stored in a desiccator until dry.

**Synthesis [complex 2] compounds Tetrapyridine-dithiocyanate-iron(II) $[Fe(NCS)_2(Py)_4]$**: The formation of the complex compound $[Fe(NCS)_2(py)_4]$ was achieved by adding 7 mL of pyridine to the iron-thiocyanate solution while purging with nitrogen gas. The mixture turned yellow after the addition of pyridine. The mixture was stirred for 30 minutes. Subsequently, the precipitate formed was filtered and washed with a pyridine and methanol solution. The resulting precipitate was stored in a desiccator until dry.

**Measurement of melting point:** The determination of the melting point and melting range was carried out using a melting point apparatus. The synthesized compound (sample) was placed into a capillary tube, and the capillary tube containing the sample was inserted into the apparatus. The apparatus was set to gradually increase the temperature. The temperature was recorded when the sample underwent a change in form from powder to a completely melted state[13].

**Measurement of the magnetic moments of complex compounds:** An empty MSB tube was weighed ($M_0$, g), and the reading of the empty MSB tube ($R_0$) was noted. The MSB tube was filled with a quantity of 0.01 - 0.1g of the synthesized crystal sample and re-weighed (M, g). The height of the sample in the tube was measured (l), typically ranging from 1-3 cm. Then, the tube was placed in the magnetic field of the MSB

balance, and the reading was recorded as (R). The value of $C_{bal}$ used was 1.14, as calculated during calibration. The magnetic susceptibility per gram of sample was calculated from the difference in readings $[(R-R_0)]$. Room temperature (T in K) was also measured. From the magnetic susceptibility data for each sample, the effective magnetic moment of the complex compound could be calculated[4].

Data calculation using the equation:

$$X_g = \frac{C_{bal} \times l \times (R_1 - R_0)}{10^9 \times (m_1 - m_0)} \dots\dots\dots\dots\dots\dots\dots\dots(1)$$

$$C_{bal} = 1.14$$

$$X_m = X_g \times Mr \dots\dots\dots\dots\dots\dots\dots\dots(2)$$

$$\mu_{eff} = 2{,}83 \sqrt{[X_m - \Delta] \times T(K)} \dots\dots\dots\dots(3)$$

## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of Iron(II) Complex Compounds

The synthesis of iron(II) complex compounds was carried out using monodentate ligands, namely, thiocyanate and pyridine ligands. The synthesis process involves mixing ligand solutions with iron(II) complexes slowly under a nitrogen gas atmosphere. The use of nitrogen gas was employed to protect the charge on the iron(II) compound, as iron compounds are prone to oxidation to iron(III). Methanol was used as the solvent for the synthesis process due to the sample's high solubility in polar solvents. The synthesized crystals can be observed in **Figure 1.**
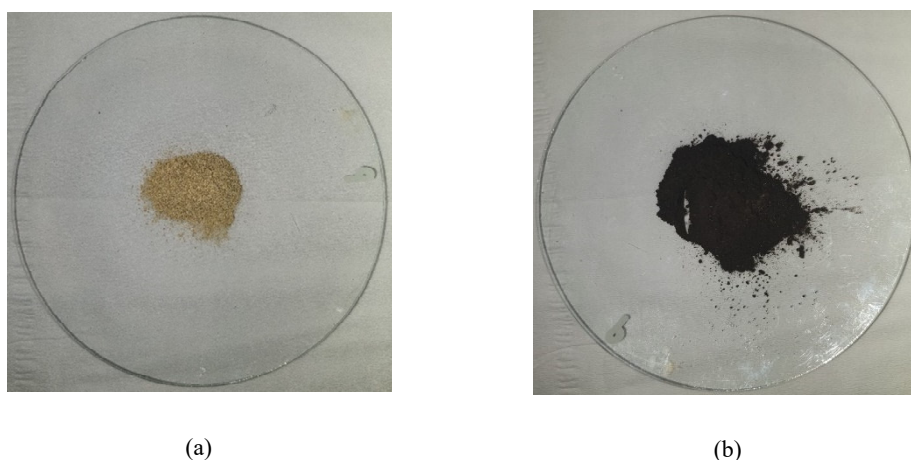


(a)                                           (b)

**Figure 1.** (a) Hexathiocyanatoiron(II) complexes; (b) Tetrapyridinedithiocyanatoiron(II) complexes

**Table 1.** Data from the synthesis of iron(II)

| NO. | Complex Compounds | Massa (g) | Yield (%) | Color |
|-----|-------------------|-----------|-----------|-------|
| 1 | $[Fe (NCS)_6]^{4-}$ | 0.1325 | 32.765 | Pale yellow |
| 2 | $[Fe(NCS)_2(py)_4]$ | 0.2567 | 52.621 | Dark purple |

From the data in **Table 1**, both crystals synthesized were initially red-orange for hexathiocyanatoiron(II) complex (**complex 1**) and bright yellow for tetrapyridinedithiocyanatoiron(II) complex (**complex 2**). However, after two days of storing both crystals in a desiccator to reduce the moisture content within the crystals, there was a change in color. Complex 1 turns pale yellow, and complex 2 turns dark purple. This color change occurs due to the desorption process of entrapped methanol[14]. The yield obtained from the synthesis of complex 1 was 32.765%, while complex 2 yielded 52.621%. The difference in yield is attributed to the addition of pyridine in complex 2, resulting in a greater quantity of crystals produced compared to complex 1, approximately 0.2567 grams. The synthesis process using pyridine ligands tends to be easier compared to using thiocyanate ligands.

Furthermore, the purity of the synthesized crystals was tested by determining their melting point. For tetrapyridinedithiocyanatoiron(II) complex compounds, the melting process began at 217°C and was complete at 219°C. Based on the purity level of a compound, it is considered pure if it exhibits a narrow temperature range of 1-2°C during the melting process. If the temperature range is greater than 2°C or less than 1°C, the observed crystal compound is considered impure[13]. The examination of the melting point range indicated that the crystals of complex 2 were pure because of their narrow melting point range, whereas for complex 1, purity results were not obtained due to limitations in the instrument for high-temperature measurements.

### 3.2 Magnetic Characterizations

The determination of the magnetic properties of complex compounds was conducted by measuring the magnetic moment using the Magnetic Susceptibility Balance (MSB). The measurement results for hexathiocyanatoiron(II) complex (**complex 1**) and tetrapyridinedithiocyanatoiron(II) complex (**complex 2**) are presented in **Table 2**.

**Table 2.** The results of magnetic moment measurements of synthesized crystal samples

| Complex Compounds | $M_0$ (g) | $R_0$ | M (g) | R | l (cm) | T (K) |
|-------------------|-----------|-------|-------|-----|--------|-------|
| $[Fe (NCS)_6]^{4-}$ | 0.7983 | -37 | 1.0082 | 252 | 3.00 | 291.15 |
| $[Fe(NCS)_2(py)_4]$ | 0.7983 | -36 | 0.8715 | 545 | 3,35 | 291.15 |

The process of measuring the magnetic moment for each sample involved weighing an empty tube ($M_0$), followed by recording the reading of the empty tube ($R_0$). The tube was then filled with the crystal sample to be measured (l), and the tube containing the crystal was re-weighed (M). The readings obtained for complex 1

were 252 (R), and for complex 2 the reading was 545 (R). Each measurement process was conducted at room temperature, which was 291.15K.

Theoretically, the magnetic moment can be calculated based on the number of unpaired electrons. This type of magnetic moment is commonly known as the spin magnetic moment ($\mu_s$)[15], An iron(II) ion with 4 unpaired electrons theoretically has a magnetic moment value of 4.89 BM and is paramagnetic in nature. Referring to research conducted by Søtofte & Rasmussen (1967), the synthesis of dithiocyanatotetrapyridineiron(II) compounds in two isomeric forms, namely the yellow compound ($\alpha$-Fepy$_4$(NCS)$_2$) and the black compound ($\beta$-Fepy$_4$(NCS)$_2$), revealed that the magnetic moment values successfully synthesized were 5.38 BM and 5.52 BM, respectively. These results were obtained through magnetic value measurements at room temperature (294.5K and 296K) with paramagnetic susceptibility ($X_{par}$) values of $24.6 \times 10^{-6}$ dan $25.8 \times 10^{-6}$ for each compound, respectively[10].

The data obtained from the calculation of the magnetic moment values for the two successfully synthesized complex compounds can be found in **Table 3**. The data from the reading of each crystal sample were used to determine the mass susceptibility values ($X_g$) (*Eq. 1*), resulting in mass susceptibility values ($X_g$) of $0.047 \times 10^{-3}$ for complex 1 and $0.030 \times 10^{-3}$ for complex 2. These $X_g$ values were then used to calculate the molar susceptibility values ($X_m$) (*Eq. 2*), yielding values of $19.047 \times 10^{-6}$ for complex 1 and $13.271 \times 10^{-3}$ for complex 2. The paramagnetic susceptibility ($X_{par}$) values were obtained by the difference between mass susceptibility and diamagnetic susceptibility. Subsequently, the magnetic moment values for each synthesized crystal were calculated using *Eq. 3*, resulting in a magnetic moment value of 6.69 BM for complex 1 and 5.61 BM for complex 2.

**Table 3.** The difference in magnetic moment values

| Complex Compounds | $X_g$ ($10^{-3}$) | $X_m$ ($10^{-3}$) | $X_{par}$ ($10^{-3}$) | $\mu_{eff}$ (BM) |
|---|---|---|---|---|
| [Fe (NCS)$_6$]$^{4-}$ | 0.047 | 19.047 | 19.246 | 6.69 |
| [Fe(NCS)$_2$(py)$_4$] | 0.030 | 13.271 | 13.488 | 5.61 |

Based on **Table 3**, the addition of thiocyanate ligands to Fe(II) metal complexes yields a larger magnetic moment compared to complexes reacted with pyridine ligands. Thiocyanate ligands are considered weak ligands that are assumed to lack the ability to separate in the *d* orbitals of Fe(II) metal ions. In other words, the hexathiocyanatoiron(II) complex is paramagnetic (high spin, hs) with an electron configuration of $t_{2g}^4 e_g^2$ where there are 4 unpaired electrons. As a result, the four *d* orbitals are no longer degenerate, and electrons occupy the lower-energy ($t_{2g}$) orbitals before filling the higher-energy ($e_g$) orbitals without pairing. In contrast, the tetrapyridinedithiocyanatoiron(II) complex exhibits diamagnetic properties (low spin, ls), the addition of pyridine ligands, acting as strong ligands in the synthesis of this compound, can push unpaired electrons in the Fe(II) metal ion to pair up. Consequently, this complex has a $t_{2g}^6$ configuration, and pyridine ligands have the ability to stabilize the low-spin state with a minimum multiplicity. This leads to a larger orbital gap between $t_{2g}$ and $e_g$, causing t$_{2g}$ orbitals to be fully occupied by electrons before electrons are added to e$_g$ orbitals[9].
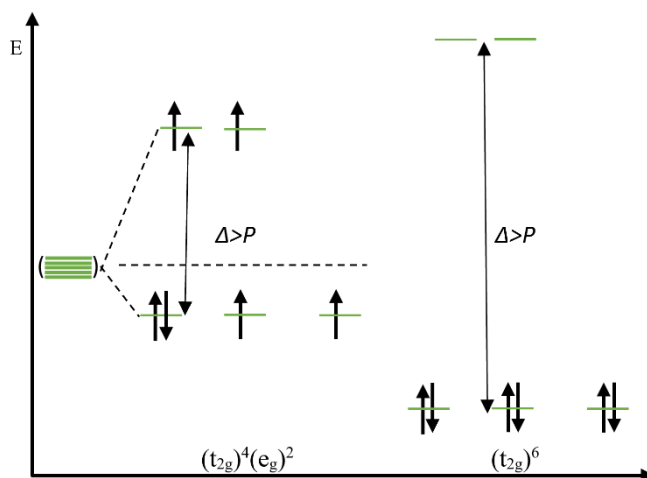
**Figure 2.** Electron configurations for Fe(II) metal ions in complex states

The differences in magnetic moment values obtained indicate the influence of ligands in the synthesis of complex compounds using transition metals. The addition of pyridine ligands demonstrates the significant influence of ligands on complex compounds, particularly on transition metal ions. The substitution of pyridine ligands in **complex 2** indicates a decrease in ligand field strength, with pyridine ligands introducing steric effects and weakening the thiocyanate ligand field strength acting on the iron atom[12]. With this condition, the ligand's ability to fill the $d$ orbitals results in a change in the magnetic properties of the Fe(II) metal ion, shifting from a paramagnetic (*hs*) state to a diamagnetic (*ls*) state. The use of ligands in this synthesis also yields a higher magnetic moment value compared to the spin magnetic moment ($\mu_s$) of the Fe(II) metal ion.

Referring to a study conducted by Ishii et al. (2008), it explains that the ligand field strength in complex form can vary based on the ligand's ability to split orbital levels in metal complexes. The results show that pyridine ligands have a greater ability compared to thiocyanate ligands in splitting orbital levels in Co(III) and Cr(III) metal complexes[8]. Nevertheless, the addition of ligands to transition metal ion complexes can have different effects on the magnetic moment value for each complex compound. The addition of ligands can also influence the magnetic properties and electron configurations of complex compounds.

## 4. CONCLUSION

The synthesis of Fe(II) metal ion complex compounds was carried out using two different types of ligands. The results showed that the crystal of hexathiocyanatoiron(II) complex, $[Fe(NCS)_6]^{4-}$ was pale yellow with a yield of 32.76%, and it exhibited a magnetic moment of 6.69 BM, measured at a temperature of 291.15K, with a resulting paramagnetic susceptibility ($X_{par}$) of $19.046 \times 10^{-3}$. The addition of thiocyanate ligands to the complex compounds played the role of weak ligands with paramagnetic (hs) magnetic properties, with an electronic configuration of $t_{2g}^4 e_g^2$. On the other hand, the addition of pyridine ligands led to dark purple crystals of tetrapyridinedithiocyanatoiron(II) complex, $[Fe(NCS)_2(py)_4]$ with a yield of 52.62% during the synthesis process. This compound had a melting point of 219°C and a paramagnetic susceptibility ($X_{par}$) of $13.271 \times 10^{-3}$ at a temperature of 291.15K, with a magnetic moment of 5.61 BM. It exhibited diamagnetic properties (ls)

with an electron configuration of $t_{2g}^6 e_g^0$. The significant difference in magnetic moments demonstrates that ligands can influence the magnetic moment, and not only that, but ligands also affect the magnetic properties and d orbital splitting in transition metal complex compounds.

## ACKNOWLEDGEMENT

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