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METAL ION COMPLEX COMPOUND Fe(III) WITH PYRAZOLINE DERIVATIVE LIGAND AS Cd(II) AND Zn(II) HEAVY METAL ION SENSOR BASED ON FLUORESCENCE

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ABSTRACT

This research aims to synthesize the complex compound of ion Fe^{3+} with para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand and its potential as the sensor of Cd^{2+} and Zn^{2+} heavy metal ions based on fluorescence. Complex compounds are characterized by a Fourier-Transform Infrared (FTIR) Spectrophotometer, Ultraviolet-Visible (UV-Vis) Spectrophotometer and Spectrofluorometer. Then, a complex compound fluorosensor study is conducted by adding Cd^{2+} and Zn^{2+} heavy metal ions using a UV-Vis Spectrophotometer and Spectrofluorometer. The results show that synthesizing the complex compound formed by reacting Fe metal and pyrazoline-derived ligands generates brown precipitate with a yield of 51.25% and a range of melting points of 252.2-253.2 ℃. The result of characterization with FTIR (cm^{-1}) generates 3380.20 (tertiary amine), 2922.31-2852.42 (C-H pyridine), 2360.38 (C=C aromatic), 1595.93-1451.88 (C=N), 1232.25-982.66 (C-N pyrazoline), 751.61-690.29 (C-H aromatic) and 366.54-339.44 (Fe-N). The Uv-Vis spectrophotometer study with a concentration of $5x10^{-5}$ M showed two absorption peaks at 246 nm, 354 nm, and 440 nm. The resulting fluorescence intensity of 813.1 a.u. At the wavelength of 500 nm. The study of complex compound fluorescence shows that the addition of Cd^{2+} heavy metal ion can be made as fluorosensor with a turn-on (enhancement) type. In contrast, the complex compound in the addition of Zn^{2+} heavy metal ion can be made as a fluorosensor with turn-off-on (quenching-enhancement) type.

Keywords: *Fluorosensor, Heavy Metal, Complex Compound, Pyrazoline Derivative.*

INTRODUCTION

Industrial and domestic activities such as public transportation allow the production of heavy metal waste [1]. Heavy metals have high toxicity, are difficult to decompose and can harm organisms in the surrounding environment. However, the body needs some essential heavy metals in small amounts [2]. Cadmium (Cd) is one of the non-essential heavy metals that cannot be used by the body and is classified as dangerous and can even cause poisoning. Zinc metal (Zn) is one of the essential heavy metals needed to maintain the body's metabolism in a non-excessive amount. If it has excessive levels, it will cause toxins in the body [3].

Photosensor is defined as sensitive to the source of certain light under appropriate conditions; in other words, material is declared a good material for photosensor application if it can provide photoluminescence (photoluminescent) by the photoluminescence of the ions it contains. Characterization, The most important property of photosensors is fluorescence sensors (fluorosensors), because characterization with fluorescence produces high selectivity and only presents components of the fluorescing ion [4]. A complex compound can be used as a fluorosensor if it is an aromatic, heterocyclic or conjugated molecule. Complex compounds can be formed because some metals and ligands form coordination covalent bonds [5].

Pyrazoline is a heterocyclic compound containing two nitrogen atoms in five rings that will coordinate with a central ion [6]. Pyrazoline and its derivatives can fluoresce and are used as ligands in complex compounds. They have been widely used to develop fluorescent probes to detect heavy metal ions, such as Zn^{2+}, Cd^{2+}, Hg^{2+}, and Cu^{2+}, based on studies that have been carried out [7-11]. The ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene is a derivative of pyrazoline which act as a free electron donor that can coordinate and chelate the central metal ion (transition metal) such as Fe, causing the formation of light absorption and emission and strong fluorescence properties [12]. So far, to the author's knowledge, no one has synthesized Fe^{3+} metal ion complex compounds with pyrazoline derivative ligands, namely para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene that is applied as a heavy metal ion fluorosensor such as Cd^{2+} and Zn^{2+}. The Fe^{3+} metal ion is used as the central atom because the Fe^{3+} ion has a very high level of stability and is a d-block transition metal that can be excited by emitting color so that it can be synthesized into complex compounds. Fe metal can also fluoresce, as in the research conducted by [13].

According to the background described above, this study is the development of previous research on complex compounds of Fe^{3+} metal ions with pyrazoline derivative ligands, namely para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene and its potential as a fluorescence-based Cd^{2+} and Zn^{2+} heavy metal sensor.

METHODS

The material used is the para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand, which the authors have previously synthesized study [11]. $FeCl_3.6H_2O$ (Merck), CH_3OH p.a (Merck), $CHCl_3$ p.a (Merck), $CdCl_2$ (Merck), and $ZnCl_2$ (Merck).

Synthesis of Complex Compound. The procedure for synthesizing Fe^{3+} metal ion complex compounds with pyrazoline-derived ligands followed the procedure reported by the authors [14], and the procedure of stoichiometric followed by Job Methode [15].

Characterization

The resulting complex compounds were characterized by Fourier Transform Infrared (Shimadzu IR Spirit), UV-Vis Spectrophotometer (Shimadzu UV-1800), fluorescence Spectrophotometer (Hitachi F-

2700 FL Spectrophotometer) and Melting Point Apparatus.

Application of Fluorosensor

After characterizing, continued fluorosensor studies of complex compounds were carried out by dissolving the compound in a 1:1 ratio of methanol and chloroform at a concentration of $5x10^{-5}$ M. The addition of heavy metal ions was carried out in a concentration range of $5x10^{-4}$ – $5x10^{-7}$ M. Before measuring the absorbance, scanning was performed to find the maximum wavelength value of the complex compound. Measurements were made in the wavelength range of 250-650 nm for the fluorescence Spectrophotometer and 190-550 nm for the UV-Vis Spectrophotometer.

RESULTS AND DISCUSSION

The analysis using the Job method [15] showed that 1 mole of Fe metal could bind 6 moles of ligands, as seen from the 1:6 ratio in Figure 1.

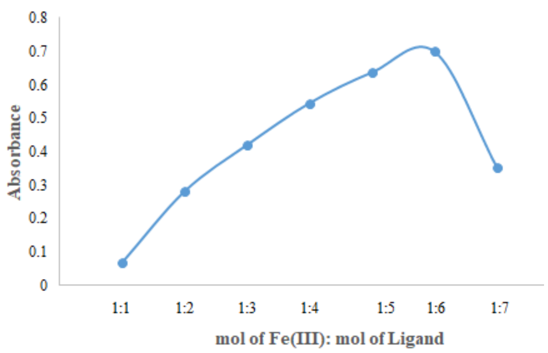


Figure 1. Job method graph.

In a 1:6 ratio, $FeCl_3.6H_2O$ metal compound and ligand were dissolved in methanol and chloroform (1:1), then stirred using a magnetic stirrer at room temperature to obtain a complex brown compound with a yield of complex compounds of 51.25 %. The melting point range of complex compounds is 252.2-253.2 °C. The result of complex compound characterization by FTIR can be seen in Figure 2.

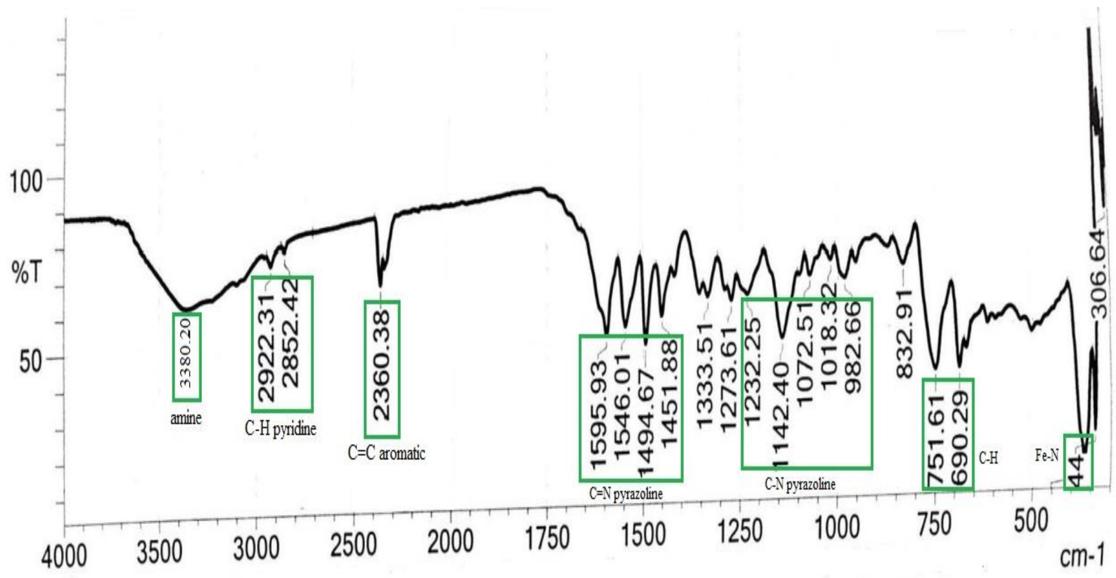


Figure 2. FTIR spectrum of complex compound

According to the spectrum in Figure 2, it can be seen that at the wave number 3380.20 cm^{-1}, there is a tertiary amine group [16]. At wave numbers 2922.31-2852.42 cm^{-1}, a C-H pyridine bond [11] and 2360.38 cm^{-1} indicate a C=C bond on the aromatic ring [17]. There are wave numbers in the area of 1595.93-1451.88 cm^{-1} indicate a C=N bond in the pyrazoline ring [18], and the presence of 1232.25-982.66 cm^{-1} indicates the presence of C-N bonds in the pyrazoline group [9], 751.61-690.29 cm^{-1} is an aromatic C-H bond [19]. At the wave number in the area of 366.54-339.44 cm^{-1}, it shows Fe-N vibrations [20].

Electronic transitions in Fe complex compounds can be detected by UV-Visible spectroscopy. The results of the characterization of complex compounds with a UV-Vis Spectrophotometer can be seen in Figure 3 and Table 1.

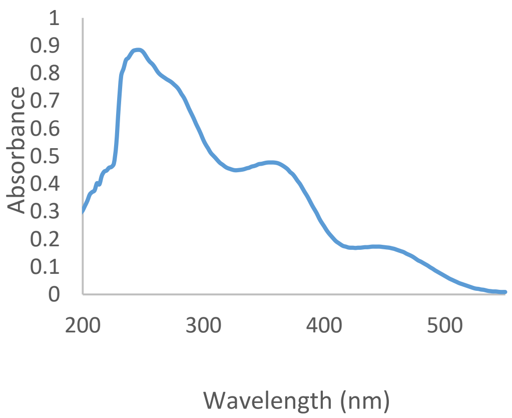


Figure 3. UV-Vis spectrum of complex compound.

Table 1. Absorbance of complex compound at a concentration of $5x10^{-5}$ M.

λ max, nm (ε, M^{-} cm^{-})	Absorbance
246 nm (17680)	0.884
354 nm (9540)	0.477
440 nm (3460)	0.173

The formation of new peaks in the spectrum of complex compounds is caused by the transition of charge transfer from metal to ligand $(\pi \rightarrow \pi *)$ [11].

The purpose of fluorescence spectrophotometer characterization was to determine the intensity of the Fe complex compound. The results in emission spectra can be seen in Figure 4.

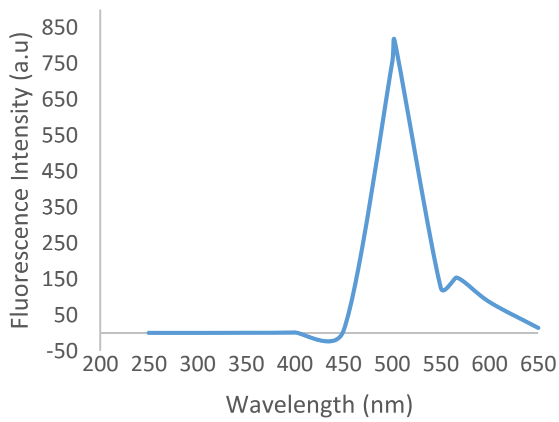
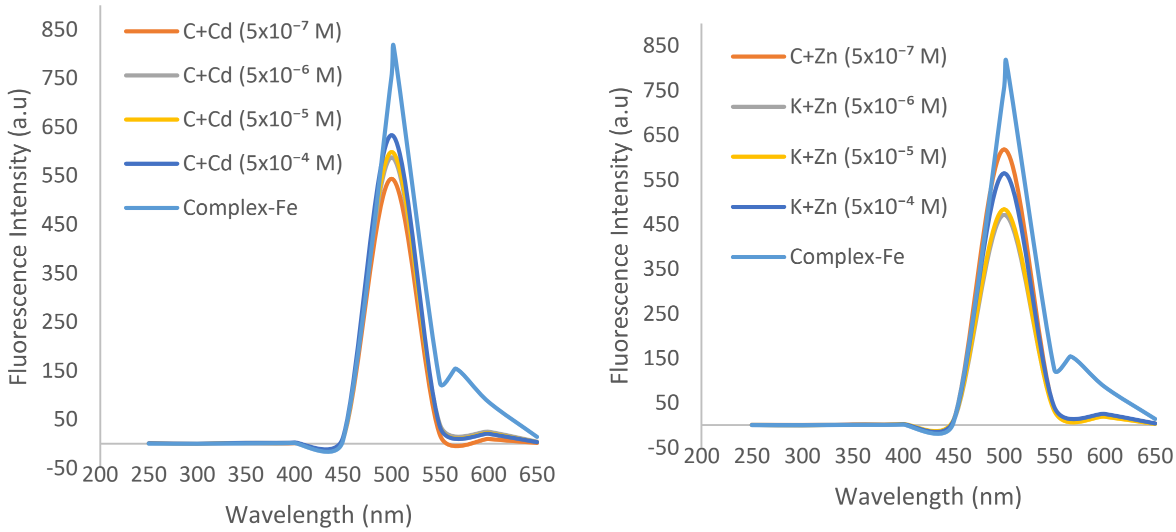


Figure 4. Fluorescence spectrum of complex compound.

Figure 4 shows the formation of one absorbance peak for the complex compound in the 500 nm region with fluorescence intensity of 813.1 a.u. It is characterized by a relatively large molar absorptivity value (ε), which means that the fluorescence intensity is also strong [21].

The results of the fluorosensor study of complex compounds on the addition of heavy metal ions Cd^{2+} and Zn^{2+} can be seen in Figure 5. The addition of heavy metal ions Cd^{2+} and at a concentration of Zn^{2+} $5x10^{-7}$ M decreased the fluorescence intensity. This is because at the time of emission, electrons in the excited energy level return to the basic state by releasing energy in the form of fluorescence (radiative emission) that is smaller than the electrons that undergo non-radiative emission, which is probably due to the small number of Cd^{2+} and Zn^{2+} ions in the complex compound.



(a) (b)

Figure 5. Fluorescence intensity spectrum of complex compounds on the addition of heavy metal ions Cd^{2+} (a) and Zn^{2+} (b) at a concentration $5x10^{-4}$ – 5 $x10^{-7}$ M.

However, with the addition of Cd^{2+} metal ions, as the metal concentration scales up, the intensity of the fluorescence complex will increase (turn on), and the lighting effect will increase with increasing metal concentration [22]. In contrast to Cd^{2+} metal ions, adding Zn^{2+} ions at a concentration of $5x10^{-6}$ M also experienced a decrease in fluorescence intensity which resulted in a quenching effect (turn off). Therefore, the fluorescence intensity will increase even more in line with the increasing Zn2+ ion concentration. From the 5x10-5 - 5x10-4 M concentration that undergoes a fluorescence intensity increase (turn on). The increase in fluorescence intensity is also due to Zn metal which is diamagnetic and can increase the fluorescence intensity [21], so it can be concluded that the fluorosensor type of Fe(III) complex compound with the addition of Zn^{2+} heavy metal ion is turned off.

CONCLUSION

The complex compounds were synthesized successfully, and a brown-coloured precipitate was obtained with a yield of 51.25 % with a melting point range of 252.2-253.2 °C. Based on the characterization results with FTIR (cm^{-1}) obtained, tertiary amine, C-H pyridine, C=N, C=C, C-N, C-H aromatic, and Fe-N. The results of UV-Vis spectroscopy characterization with a concentration of $5x10^{-5}$ M obtained three absorption peaks at 246, 354, and 440 nm. The results of the fluorescence spectrophotometer characterization of complex compounds obtained a fluorescence intensity of 813.1

a.u. at a wavelength of 500 nm. The study of fluorosensor complex compounds shows that the addition of heavy metal ions Cd^{2+} can be used as a turn-on type fluorosensor. In contrast, complex compounds with the addition of Zn^{2+} heavy metal ions can be used as a turn-off-on type fluorosensor.

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