Hg(II) and Cd(II) Heavy Metal Ions Detection Based On Fluorescence Using Zn(II) Metal Ion Complex with Pyrazoline Derivatives Ligand

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Article history: *received 08 April 2022; revised 22 Mei 2022; accepted 29 Juni 2022; published 30 Juni 2022*

Abstract

Pyrazoline derivatives can be used as ligands because they have photophysical properties and can chelate metal ions which cause very strong absorption, emission, and have a fluorescence properties. Therefore, in recent years, pyrazoline ligands and their derivatives have been widely used for chemosensors. This research aims to detect fluorescence-based heavy metal ions Hg^{2+} and Cd^{2+} using a metal ion complex compound Zn^{2+} with pyrazoline derivative ligand. The research was started by synthesizing pyrazoline-derived ligands, then synthesizing complex compounds. Complex compounds were characterized using Fourier Transform Infra Red (FTIR), UV-Vis Spectrophotometer, and Spectrofluorometer. Then, a fluorescence study was carried out to determine the type of fluorosensor for complex compounds with the addition of heavy metal ions Cd^{2+} and Hg^{2+}. The last stage was UV-Vis spectroscopy study on the addition of heavy metal ions Hg^{2+} and Cd^{2+}. Pyrazoline derivative ligand obtained as para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene was a yellow solid. The metal ion complex compound Zn^{2+} with pyrazolin derivative ligand was a brown colored compound, has a yield of 55% and a melting point was 245 ºC. The FTIR spectrum showed the presence of functional groups such as amine, C-H aromatic, C=N, C=C aromatic, C-N, Zn-N, and Zn-Cl. Analysis with UV-Vis spectrophotometer showed that there was a shift in the maximum wavelength from the ligand to the Zn(II)-ligand complex, namely 240 nm to 246 nm and 363 nm with molar absorptivity values (log ε) of 4.56 and 4.28, respectively. For fluorescence analysis, two absorbance peaks were obtained, namely at a wavelength of 370 nm and 478 nm with an intensity of 3644 a.u and 8216 a.u, respectively. The results of fluorescence chemosensor studies on the addition of heavy metal ions Hg^{2+} and Cd^{2+} showed that the metal ion complex compound Zn^{2+} with pyrazoline-derived ligands can detect heavy metal ions Hg^{2+} and Cd^{2+} with a turn-on type.

Keywords: Fluorescence, Pyrazoline, Zinc, Mercury, Cadmium.

1. INTRODUCTION

Indonesia is one of the countries that experiences a significant increase in the number of transportation and industry every year. The impact of the large use of land transportation and the presence of industry allows the production of heavy metal waste [1]. In general, heavy metals have high toxicity, are difficult to decompose and can harm organisms in the surrounding environment. However, some essential heavy metals are needed by the living body in small amounts [2]. According to Istarani & Ellina (2014), heavy metal pollutants have serious problems. Cadmium (Cd) and mercury (Hg) are the most common heavy metal ions because they have harmful effects [3]. So that the detection of heavy metal ions of cadmium and mercury was carried out. Pyrazoline derivatives function as ligands because they have photopysical properties and can chelate metal ions by donating a lone pair of electrons and providing energy to the metal ion. Chelation of metal ions with pyrazoline-derived compounds can cause the formation of absorption and emission of light that is so strong and has fluorescence properties caused by the presence of a lone pair of electrons on the ligand which acts as light that can absorb the chromophore [4]. The used of metal ions Zn^{2+} as a central atom because the Zn^{2+} ion has a very high level of stability and was a d-block suborbital transition metal that can be excited by emitting color so that it can be synthesized into complex compounds and Zn^{2+} metal can also fluoresce [5]. Thus, it is possible that complex compounds with a central Zn^{2+} atom as well as pyrazoline-derived ligands can be used for fluorescence. Fluorescence-based compound detection (fluorosensor) has been widely used and is becoming popular in biochemistry, forensics, and heavy metal detection fields. This is because fluorosensors or fluorescence-based

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e-ISSN: 2776-4508; p-ISSN: 2686-1038
Publisher : Universitas Pakuan

sensors offer good selectivity, low detection limits and practical applications [6].

Complex compounds can be used as fluorosensors if they are heterocyclic compounds, aromatic compounds, or conjugated molecules. Complex compounds are formed when there are metals and ligands that form coordination covalent bonds [5]. The ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene is a pyrazoline-derived ligand of heterocyclic compounds containing two nitrogen atoms in a five-membered ring [7].

Jung et al (2017) has succeeded in synthesizing zinc complex for detecting Hg(II) and hydrosulfide, which gives the results that the zinc complex can detect Hg(II) and hydrosulfide with a turn-off fluorosensor type [8]. Sharma et al (2022) has succeeded in synthesizing pyrazoline derivative 5-(4-methylphenyl)-3(5-methylfuran-2-yl)-1-phenyl-4,5-dihydro-1H-pyrazole, and its application for detection of Cd^{2+} ion as turn-off fluorescent sensor [9]. However, there are no studies that explain the use of metal ion complex compounds Zn^{2+} with pyrazoline-derived ligands specifically para-di-2(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene that can be used as fluorosensors to identify the presence of mercury and cadmium ions . The authors use the metal ion Zn^{2+} as the central atom because the Zn^{2+} ion has a very high level of stability and is a d-block suborbital transition metal that can be excited by emitting color so that it can be synthesized into complex compounds and Zn^{2+} metal can also fluorescence. Based on this background, this study aims to detect fluorescence-based heavy metal ions Hg^{2+} and Cd^{2+} using a metal ion complex compound Zn^{2+} with pyrazoline-derived ligands.

2. METHODS

2.1 Equipment and Materials

In this research, the equipment used are beaker, watch glass, stirring rod, volumetric pipette, bulb, boiling flask, micropipette, magnetic stirrer, vial, whatman filter paper, desiccator, hotplate, analytical balance, rotary evaporator, universal indicator, UV-Vis spectrophotometer (Shimadzu UV-1800), FTIR (Shimadzu IR Spirit), Fluorescence spectrophotometer (Hitachi F-2700) and Melting Point Apparatus (RY-2). The materials used in this study were the ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro1H-pyrazole-5-yl)benzene, chloroform p.a (Merck), methanol p.a (Merck), zinc(II) chloride (Merck), mercury(II) chloride (Merck), cadmium(II) chloride (Merck), hydrochloric acid p.a (Merck), and sodium hydroxide p.a (Merck).

2.2 Synthesis and Characterization of Zn^{2+} Metal Ion Complex Compounds With para-di-2(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligands [10]

A total of 1 mmol of the synthesized ligand and 1 mmol of $ZnCl_2$ were dissolved in 20 mL of different p.a methanol. Then the two solutions were mixed and stirred with a magnetic stirrer for 35 minutes at room temperature and pressure. The resulting solution and precipitate are yellowish brown in color. Then the precipitate was filtered and washed using cold methanol and hexane as solvent to stand in a desiccator [10]. The resulting complexes were characterized using FTIR, UV-Vis, Fluorescence Spectrophotometer, and Melting Point.

2.3 Fluorescence Experiment

Measurement of the fluorescence intensity of complex solutions with the addition of metal ions Hg^{2+} and Cd^{2+} was used to determine the optimum concentrations of metals Hg^{2+} and Cd^{2+} which can cause a decrease or increase in the maximum fluorescence intensity. The complex compound at a concentration of $5x10^{-5}$ M was dissolved in methanol and chloroform (1:1), then metal ions Hg^{2+} and Cd^{2+} were added in the concentration range from $5x10^{-7}$ M to $5x10^{-4}$ M. Next was scanned at a wavelength of 220-550 nm. The results obtained were plots of emission and excitation intensity with respect to wavelength. This measurement was used to determine the selectivity of complex compounds on the addition of heavy metal ions Hg^{2+} and Cd^{2+}.

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of Complex Compound

The ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene was a derivative of pyrazoline compound which was yellow in color with a melting point of 230.9 °C. The synthesis of $ZnCl_2$ complex compounds with pyrazoline-derived ligands produced a brown solid and obtained a yield of 55% with a melting point of 245.0 °C. Analysis

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e-ISSN: 2776-4508; p-ISSN: 2686-1038
Publisher : Universitas Pakuan

of ligand and complex compounds using FTIR instruments aims to determine the functional groups of complex compounds can be seen in Figure 1.

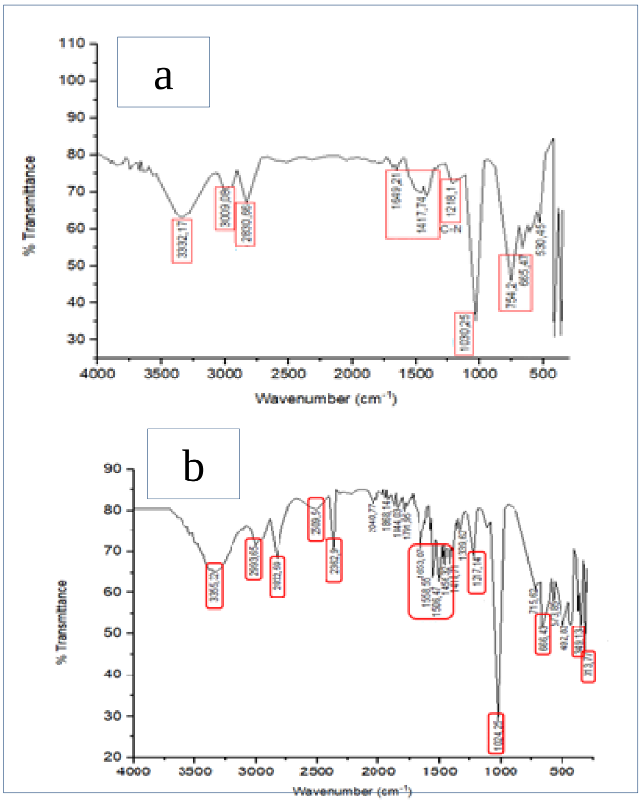

Figure 1. FTIR Spectrum of Ligand (a) and Complex Compound Zn^{2+} with Ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene (b)

Based on the spectrum in Figure 1, it can be concluded that the wavenumber shift that occurs between the ligands and Zn complex compounds is shown in Table 1 below.

Tabel 1. Results of FTIR analysis of pyrazoline ligands and Zn^{2+} complex compounds

Bond	Wave number (cm^{-1})	
	Pyrazoline Ligand	Zn^{2+} Complex
Amine	3332,17 [11]	3355,32 [12]
C-H Aromatic	665,47-754,2 [11]	666,43 [11]
C=N	1417,74-1649,21 [13]	1456,32 [12]
C=C Aromatic	2830,66 [11]	2832,59 [14]
C-N pyrazoline	1218,1 [11]	1217,14 [12]
C-N pyridine	1030,25 [11]	1024,25 [11]
C-H pyridine	3009,08 [15]	2993,65 [11]
Zn-N	-	349,13 [16]
Zn-Cl	-	313,77 [17]

Based on Table 1, there was a shift in the wavenumber of the ligands after the addition of the Zn^{2+} complex compound, this indicates that the complex compound has been bound by the pyrazoline ligand.

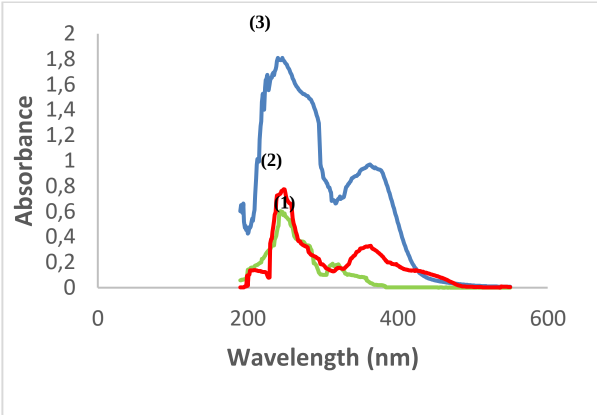

Figure 2. Spectrum of UV-Vis: (1) $ZnCl_2$, (2) ligand, (3) Zn^{2+} complex

UV-Visible analysis of this complex compound aims to determine the formation of a shift in the maximum absorption peak as well as an increase or decrease in the absorption intensity. The shift in maximum wavelength from the ligand to the Zn(II)-ligand complex can be seen in Figure 2 and Table 2. This wavelength shift indicates that there is an electrostatic interaction between ligands that have a lone pair of electrons and complex compounds that have zinc metal ions [6].

Table 2. Results of Maximum Wavelength Analysis

Analysis	Maximum Wavelength (nm)
Ligand	249 364
$ZnCl_2$	243 367
Zn(II)-Ligand	246 363

Electron transition of $\pi \rightarrow \pi^*$ characterized by relatively large molar absorptivity values (ε), this can be seen in both absorption peaks (Table 3). The relatively large value of the molar absorptivity (ε) indicates that this compound has a strong fluorescence intensity [18].

In this study, observations were made on the fluorescence characteristics of the Zn^{2+} complex compound with the ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene, which is shown in Figure 3.

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e-ISSN: 2776-4508; p-ISSN: 2686-1038
Publisher : Universitas Pakuan

Table 3. UV-Visible Absorption Peak of Zn^{2+} Complex Compound

λ maks, nm (ε, $M^{-}cm^{-}$)	Absorbance	Log ε
363,0 nm (19388)	0.9694	4.28
246,0 nm (36196)	1.8098	4.56

Based on Figure 3, the results were in the form of an emission spectrum with the formation of two absorbance peaks for complex compounds, namely in the 370 nm area, which was an excitation absorption peak with a fluorescence intensity of 3644 a.u and in the 478 nm region an emission absorption peak with a fluorescence intensity obtained of 8216 a.u. At a maximum wavelength of 370 nm, the fluorescence intensity is lower than at a maximum wavelength of 478 nm, this is because there was one type of electronic transition that occurs when UV light hits the complex, in the emission process, electrons at one of the excited energy levels at a maximum wavelength of 370 nm return to their ground state without releasing energy in the form of non-radiative emission (fluorescence) [19].

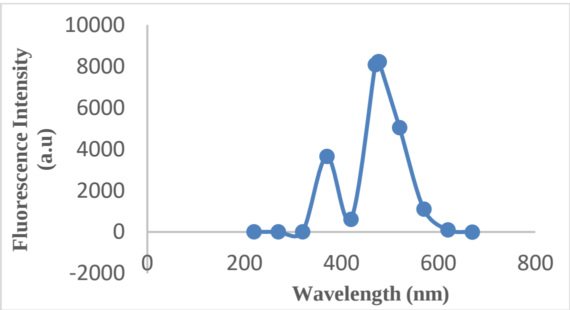

Figure 3. Fluorescence Spectrum of Zn^{2+} Complex Compound

3.2 Fluorescence Studies

At the fluorescence intensity of the complex compound Zn^{2+} with the addition of heavy metal ion Hg^{2+} at various variations, the maximum emission wavelength of the complex compound was measured at 500 nm. The Hg^{2+} ion was a diamagnetic metal which tends to increase the fluorescence intensity. The interaction of the ligand with metal ions Hg^{2+} can produce lighting which causes an increase in fluorescence in the maximum absorption region [19].

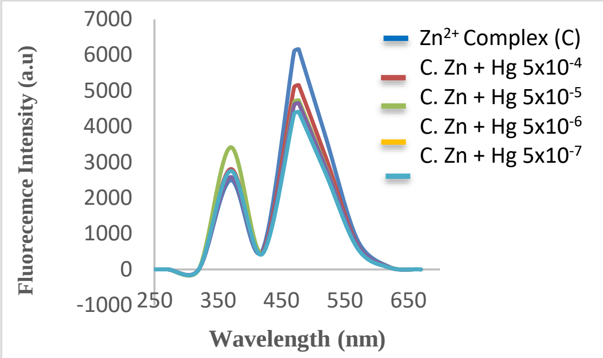

Figure 4. Fluorescence Intensity Spectrum of Complex Compounds on the Addition of Heavy Metal Ions Hg^{2+} at Various Concentrations

Figure 4 shows that the Zn^{2+} complex compound with the addition of heavy metal ions Hg^{2+} at a concentration of $5x10^{-7}$ M – $5x10^{-4}$ M experienced an increase in fluorescence intensity (turn on), which means that the lighting effect increases with increasing Hg^{2+} ion concentration. There was also a slight shift in wavelength with the addition of Hg^{2+} ions, indicating an interaction between the complex compound Zn^{2+} and Hg^{2+} ions at a wavelength of 476 nm to 477 nm and 370 nm to 371 nm. In addition, there are two absorption peaks in the 370 nm and 477 nm regions, this happens because when the electron returns to the ground state, the electron first occupies a higher energy level in the ground state before dropping to a lower level [13].

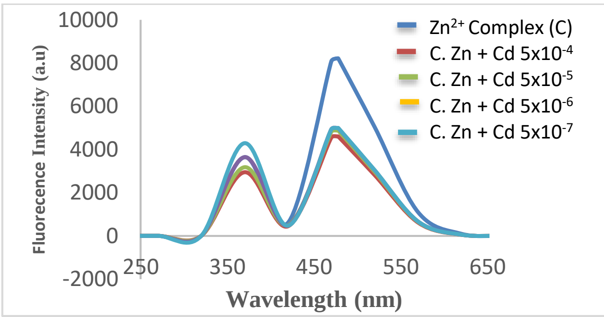

Figure 5. Fluorescence Intensity Spectrum of Complex Compounds on the Addition of Heavy Metal Ions Cd^{2+} at Various Concentrations

The magnetic properties of a metal quite affect the fluorescence intensity of the ligands. Like the Hg^{2+} metal ion, the Cd^{2+} ion is also a diamagnetic metal which tends to increase the

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e-ISSN: 2776-4508; p-ISSN: 2686-1038
Publisher : Universitas Pakuan

fluorescence intensity. The interaction of the ligand with metal particles of cadmium (Cd) which can produce lighting that causes fluorescence to increase at maximum absorption [19]. In Figure 5 there was a slight shift in wavelength indicating the interaction between the complex compound Zn^{2+} and Cd^{2+} ions at a wavelength of 478 nm to 477 nm and 370 nm to 371 nm. Beside that the figure also shows Zn^{2+} complex compound with the addition of Cd^{2+} heavy metal ions at a concentration of $5x10^{-7}$ M – $5x10^{-4}$ M experienced an increase in fluorescence intensity (turn on) because the lighting effect increased with increasing metal concentration added. Just like the addition of Hg^{2+} ions, the addition of Cd^{2+} ions there are two absorption peaks in the 370 nm and 478 nm regions, this happens because when the electron returns to the ground state, the electron first occupies a higher energy level found in the ground state before dropping to a lower level [13].

4. CONCLUSION

Based on the results of the research that has been carried out, it can be concluded that the synthesis of the metal ion complex Zn^{2+} with the ligand para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene resulted in a yield of 55% and fluorescence intensity of 3644 a.u and 8216 a.u. at a wavelength of 370 and 478 nm, respectively, and the log molar absorptivity of 4.28 and 4.56, respectively. The results of the fluorosensor study produced a metal ion complex compound Zn^{2+} with pyrazoline derivative ligands which have the potential to be used as a turn-on type of Hg^{2+} and Cd^{2+} metal ion fluorosensor. This heavy metal fluorosensor can detect the presence of Hg^{2+} and Cd^{2+} ions to a low concentration of $5x10^{-7}$ M.

ACKNOWLEDMENT

We would like to thank LPPM Universitas Pakuan for funding and supporting this research so that this research can be carried out

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