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FLUOROSENSOR OF Hg^{2+} AND Cu^{2+} HEAVY METAL IONS FROM COMPLEX COMPOUND OF Co^{2+} AND para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene LIGAND

Yulian Syahputri* and Linda Jati Kusumawardani

Department of Chemistry, Mathematics and Natural Science Faculty, Universitas Pakuan
Jl. Pakuan PO Box 452 Bogor. West Java 16143, Indonesia

* For correspondence purposes, tel/fax : 081381149591, email: syahputri.yulian@unpak.ac.id

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ABSTRACT

Industrial activities like waste disposals and domestic activities may produce heavy metal waste like Hg^{2+} and Cu^{2+}. The purpose of this research is to synthesize the complex compound of metal ion Co^{2+} and para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand and its potentials as the fluorosensor of Hg^{2+} and Cu^{2+} heavy metal ions. Complex compounds are characterized with a fourier-transform infrared (FTIR), ultraviolet-visible (UV-Vis) spectrophotometer, and spectrofluorometer. After that, a complex compound fluorosensor study is conducted by adding Hg^{2+} and Cu^{2+} heavy metal ions using a spectrofluorometer. The results show that the synthesis of complex compound generates brownish-yellow sediment with a yield of 36% (melting point of 243.2°C). The result of characterization with FTIR (KBr, cm^{-1}) generates 3060.65 (C-H aromatic), 2851-2919.46 (C-H pyridine), 2363.23 and 1640.14 (C=N), 1493.24-1594.5 (C=C), and 1326.38-1019.74 (C-N). The result of UV-Vis spectrophotometer scanning obtains two absorption peaks on 250 nm and 366 nm in the concentration of $5x10^{-5}$ M. The resulting fluorescence intensity of 1150 a.u. At the wavelength of 470 nm. The study of complex compound fluorescence shows that the addition of Hg^{2+} heavy metal ion can be made as fluorosensor with turn-on type. In contrast, the addition of Cu^{2+} ion can be made fluorosensor with turn-off type.

Keywords: *Fluorosensor, Cobalt Metal, Complex Compound, Pyrazoline*

INTRODUCTION

Industrial activities like waste disposals may produce wastes in the form of heavy metals. Moreover, domestic activities like public transportation and fisherman boats may also make heavy metal wastes [1]. Heavy metal commonly has a toxic property and is hazardous for organisms even though some are necessary for small amounts. Copper ion (Cu) is a heavy metal ions essential for the human body and acts for physiological processes in appropriate amounts [2]. Heavy metal like mercury (Hg) is considered the most hazardous metal ion for the environment since it widely spreads in the air, water, and soil. It occurs since mercury will be easily and quickly accumulated in the environment and contaminate water and foods [3].

The detection of Hg^{2+} and Cu^{2+} heavy metal ions plays an essential role in chemistry and biology, which will have a major impact on human health and the environment in heavy metal testing [4]. It occurs since heavy metals are pollutants that cannot be degraded or destroyed to accumulate in nature and organism bodies [5]. The detection based on fluorescence (fluorosensor) will result in turn-on fluorescence intensity or an increase in fluorescence intensity and turn-off or a decrease in fluorescence intensity [6]. The advantage of fluorosensors is that they offer good selectivity and low detection limits with practical applications.

Synthesized the derivative of pyrazoline 1,3,5-Triaryl-2-pyrazolines used as a fluorosensor for Cu^{2+}metal and produces a "Turn-Off" type fluorosensor [7]. Synthesized a complex compound from $CoCl_2.6H_2O$ metal with acetylacetonate ligand [8]. Pyr-Ryn with pyrazole derivatives and shows the response of a "Turn-On" type fluorosensor to Hg^{2+} metal ion [9].

Complex compounds can be used as fluorosensors if they are aromatic compounds, heterocyclic compounds, or conjugated molecules. A complex compound can be formed due to metals and ligands that form coordination covalent bonds [10]. The para-di-2-(1-methyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand is included in the pyrazoline derivative, which is a heterocyclic compound containing two nitrogen atoms in a five-membered ring [11]. This compound may form complexes since it has two donor atoms, i.e. two N atoms that can coordinate with the central atom, namely Co metal. In addition, pyrazoline-based ligands have good photo-physical properties and ease of synthesis [6].

So far, based on the knowledge of the author, no one has synthesized complex compounds between pyrazoline derivative and $CoCl_2.H_2O$ metal, which is used as a fluorosensor for Hg^{2+} and Cu^{2+} heavy metal ions. The Co^{2+} complexes are widely used since the transitional metals in the first series can form stable and fluorescent complexes.

METHODS

Materials which used are the para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand that has been synthesized, cobalt (II) chloride hexahydrate (Merck p.a), mercury (II) chloride (Merck p.a), copper (II) chloride dihydrate (Merck p.a), methanol (Merck p.a), chloroform (Merck p.a), diethylether (Merck p.a), hydrochloric acid (Merck p.a) and sodium hydroxide (Merck p.a).

The instruments used are fluorescence spectrophotometer (Hitachi F-2700), UV-Vis spectrophotometer (Genesys 10uv scanning), Fourier-Transform Infrared (Shimadzu IRSpirit), and Melting Point Apparatus.

The synthesis procedure of the complex compound from Co^{2+} metal ion with para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand follows the synthesis procedure previously reported by the authors [12]. Infrared spectrophotometer, ultraviolet-visible spectrophotometer both characterize the resulting complex com-pounds. Spectrofluorometer, then continued with fluorosensor studies on heavy metal ions Hg^{2+} and Cu^{2+} using an ultraviolet-visible spectrophotometer and a spectro-fluorometer. The fluorosensor study is initiated by measuring the fluorescence intensity of the complex compound dissolved in methanol and chloroform with the ratio of 1:1 at a concen-tration of $5x10^{-5}$ M. Before measuring;

scanning is conducted to find the maximum wavelength. Measurements are conducted in the 220-550 nm wavelength range.

The fluorescence intensity measurement is then continued to determine the optimal concentration of Hg^{2+} and Cu^{2+} metals, which may cause a decrease or increase in fluorescence intensity. Complex compounds at the concentration of $5x10^{-5}$ M are dissolved in chloroform and methanol in the ratio of 1:1 then added with Hg^{2+} metal ion in the concentration range of $5x10^{-7}$ to $5x10^{-4}$ M. The same is applied to Cu^{2+} metal ion. Scanning is conducted at the wavelength of 220-550 nm (spectrofluorometer) and the wavelength of 190-550 nm (ultraviolet-visible spectrophotometer).

RESULTS AND DISCUSSION

The synthesis of complex compounds is initiated by dissolving $CoC_{12}.6H_2O$ metal in methanol, producing a purplish red solution, while a para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand is dissolved in chloroform, producing a yellowish-brown solution. Both are mixed with a yellowish-brown solution and stirred using a magnetic stirrer for ± 30 minutes. After the stirring is complete, the solvent in the solution is then removed using rotatory evaporation at the temperature of 60°C and then cooled before washing. The washing process is carried out using methanol (5 mL) and diethyl ether (10 mL) and generates a yellowish-brown complex compound with a complex yield of 36% and a melting point of 243.2°C.

1. FTIR Analysis of Complex Compound

Analysis of complex compounds by FTIR aims to determine the functional groups of complex compounds. Based on the spectrum in Figure 1, the C-H aromatic bond is seen at wave number 3060.65 cm^{-1} and wave number 2919.46-2851 cm^{-1} due to the widening of C-H aromatic in the pyridine ring [13]. The waves in the regions of 1640.14 and 2363.23 cm-1 indicate C=N bonds in the pyrazoline group [14].

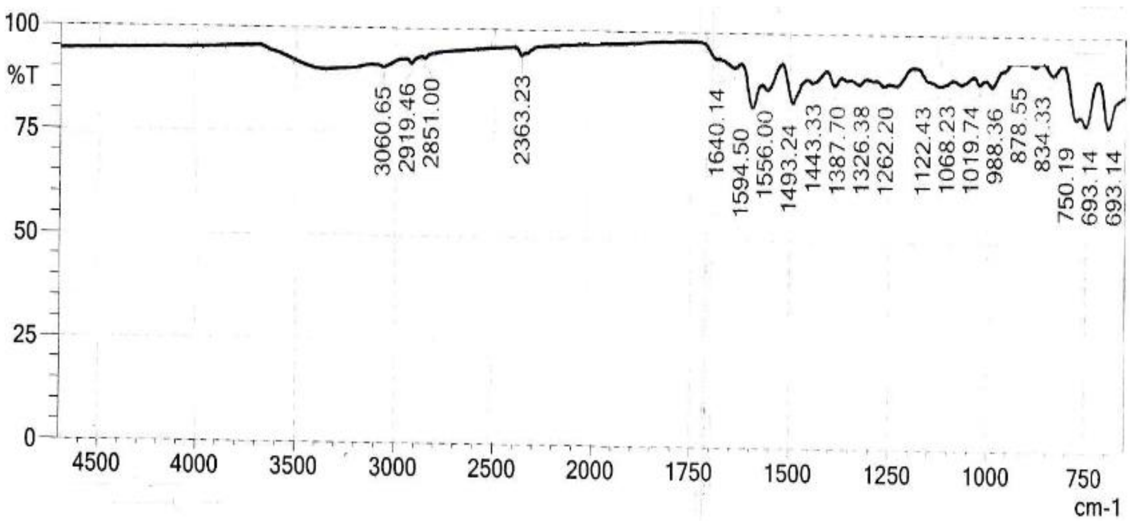

Figure 1. FTIR spectrum on the complex compound of Co^{2+} metal ion and para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand.

The appearance of the wavenumbers in the area of 1594.50-1493.24 cm^{-1} is caused by the C=C vibration in the aromatic ring. The wavenumbers in the regions of 1326.38-1019.74 cm^{-1} indicate the presence of C-N bonds in the pyrazoline group [13] [14].

2. UV-Vis Analysis of Complex Compound

The formation of complex compounds begins with scanning wavelengths and then determining the maximum wavelengths to discover the wavelength of the para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand, cobalt (II) metal ion, and complex compounds. The maximum wavelengths of ligands and complexes are determined in the range of 190-550 nm. After dissolving it with methanol as a solvent, the maximum wavelength of the purplish-red cobalt (II) metal ion is determined with the range of 380-600 nm.

The shift of the peak towards the larger wavelength, as seen in Figure 2, is an early indication that the complex is formed. This wavelength shift indicates an electrostatic interaction between ligands with lone pairs and complex compounds containing cobalt metal ion [15].

Based on Figure 2, the UV-Vis spectrum of the complex shows two absorption bands. First is at the maximum wavelength of 250 nm with the absorbance value of 1.399 and the molar absorptivity value (Log ε) of 4.44. The second is at the maximum wavelength of 366 nm with the absorbance value of 0.860 and the molar absorptivity value (Log ε) of 4.23. The π - π* electron transition is characterized by a relatively high molar absorptivity value (ε), and it is seen at both absorption peaks. The relatively high molar absorptivity value (ε) also indicates that this compound has strong fluorescence intensity [15].

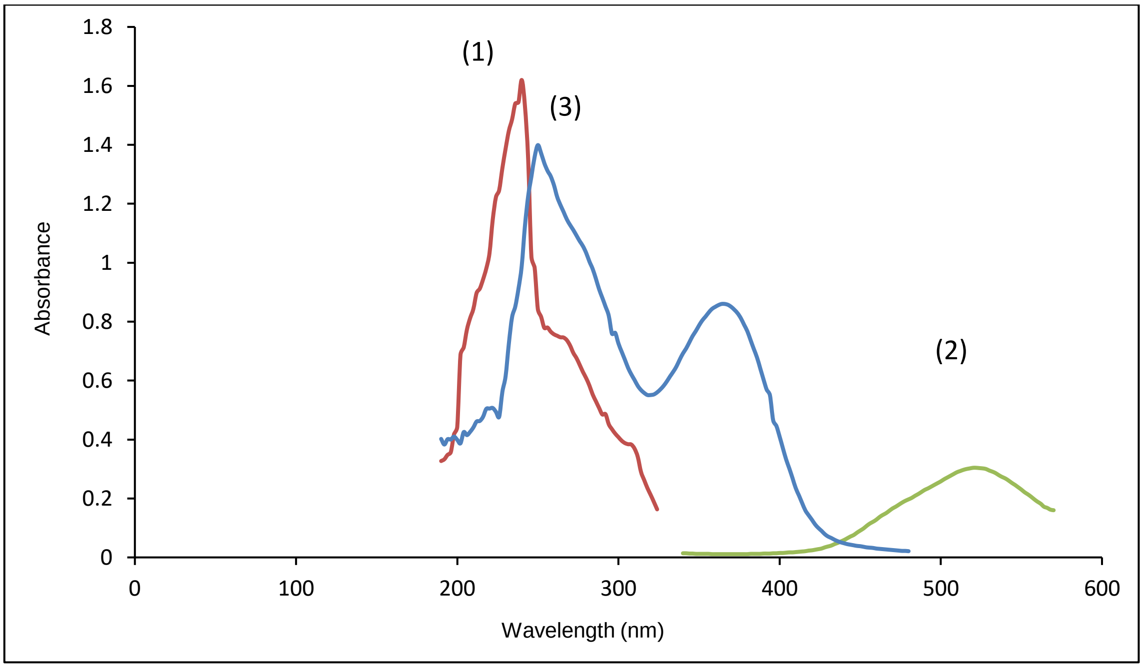

Figure 2. UV-Vis spectra: (1) para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand solution; (2) $CoCl_2.6H_2O$ solution, and (3) complex compound solution.

3. Fluorescence Analysis of Complex Compound

The characterization of the complex compound by Spectro fluorescence results in an emission spectrum chart, as shown in Figure 3.

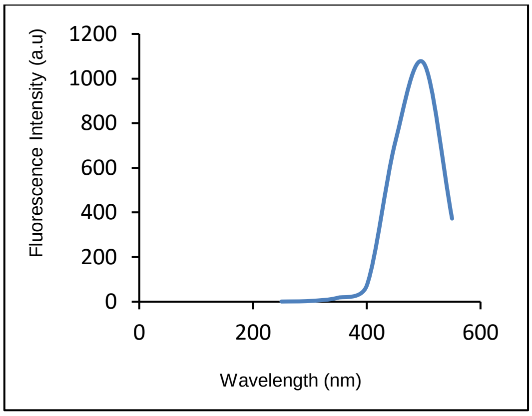

Figure 3. Fluorescence spectrum of complex compound.

Based on Figure 3, there is one absorption peak of complex compounds in the area of 470 nm with fluorescence intensity of 1150 a.u. It is in line with the data on the characterization result of complex compounds using a UV-visible spectrophotometer. The complex compound has a high molar absorptivity value, meaning that its fluorescence intensity is high [15].

4. UV-Visible Study of Complex Compound with the Addition of Hg^{2+} and Cu^{2+} Heavy Metal Ions

The effect of adding heavy metal ions to complex compounds is observed by UV-Visible spectroscopy. Measurements are conducted in which a complex compound is added with Hg^{2+} and Cu^{2+} ions by varying the metal ion concentration. The effect of adding Hg^{2+} ion is shown in Figure 4

Figure 4 shows a complex compound, with the addition of Hg^{2+}ion, undergoes an exchange between the Hg^{2+} ion and the Co^{2+} ion by forming a new complex with the Hg^{2+} ion. It indicates a shift in wavelength to a lower wavelength, from 250 nm to 234 nm [16]. The effect of adding Cu^{2+} metal ion to the complex compound is seen in Figure 5.

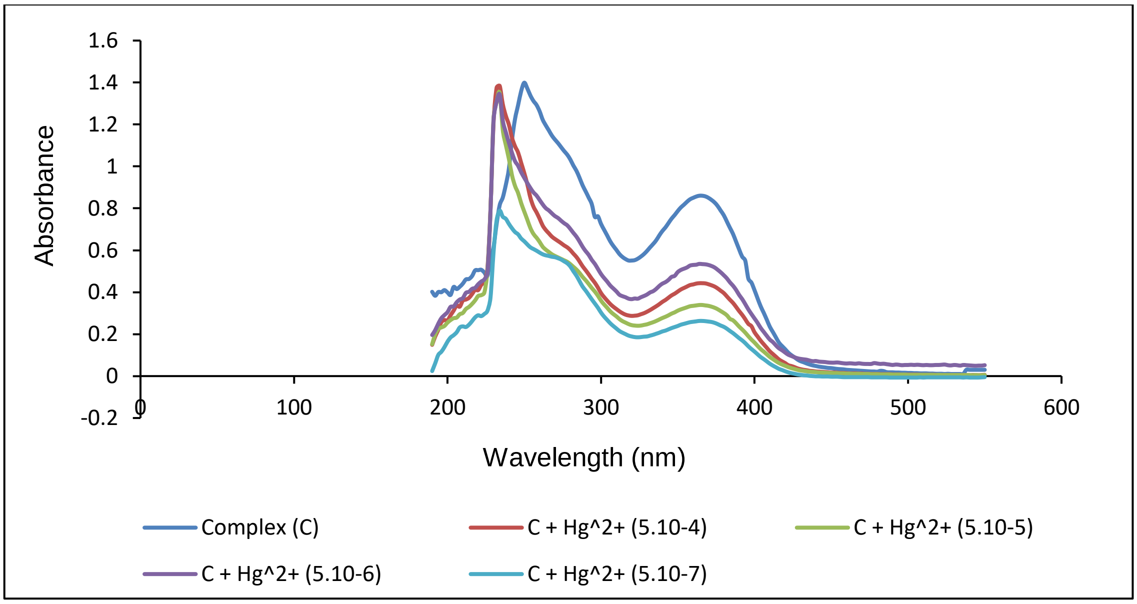

Figure 4. Chart on the effect of Hg^{2+} heavy metal ion addition against various concentrations of complex compound.

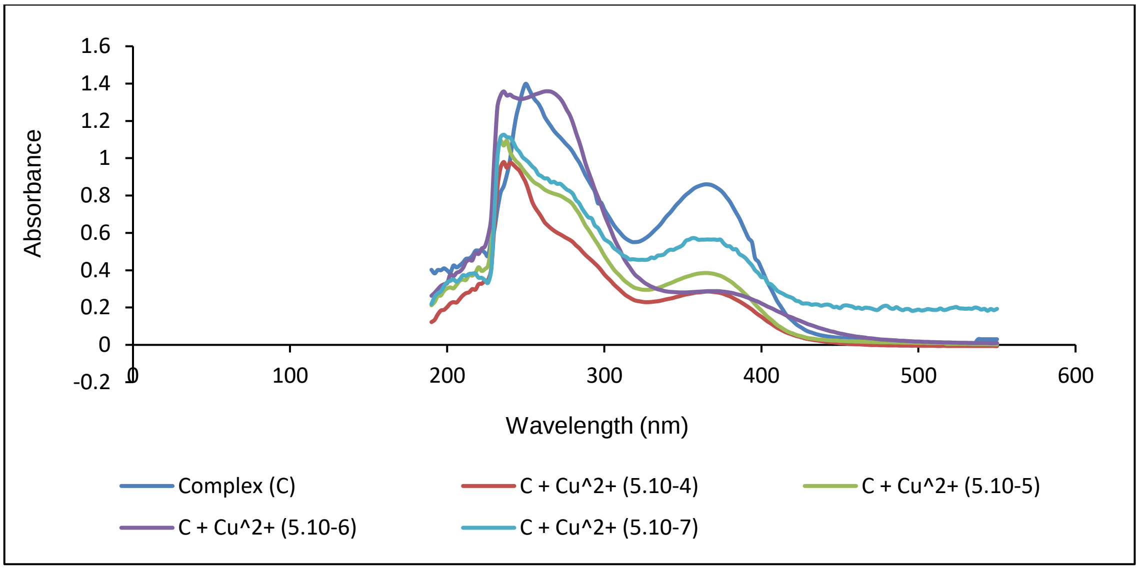

Figure 5. Chart on the effect of Cu^{2+} heavy metal ion addition against various concentrations of complex compound.

Figure 5 shows a complex compound, with the addition of Cu^{2+} ion, undergoes an exchange between Cu^{2+} ion and Co^{2+} ions by forming new complexes with Cu^{2+} ion. It indicates a shift in wavelength to a lower wavelength, from 250 nm to 238 nm.

5. Study of Complex Compound Fluorescence with the Addition of Hg^{2+} Heavy Metal Ion

The addition of Hg^{2+} metal ion is carried out at the concentration of $5x10^{-7}$-$5x10^{-4}$ M into a complex compound with $5x10^{-5}$ M in methanol-chloroform solvent (1:1). The fluorescence intensity of complex compounds with the addition of Hg^{2+} metal ion is seen in Figure 6.

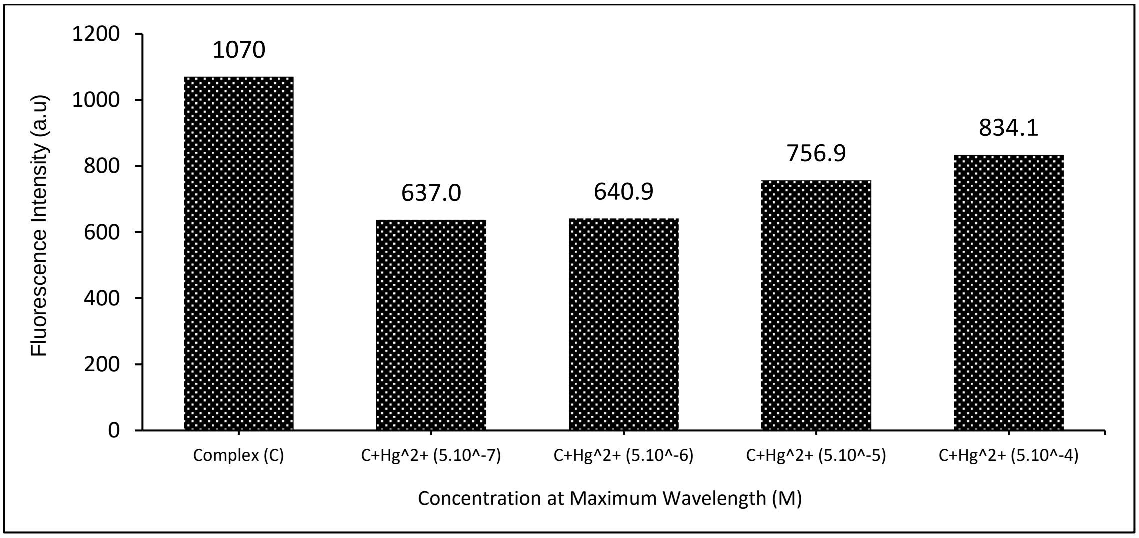

Figure 6. Chart on change in the fluorescence intensity of complex compounds against the addition of Hg^{2+} heavy metal ion at various concentrations.

The fluorescence intensity of complex compounds, on the addition of Hg^{2+} metal ions at a maximum complex wavelength of 470 nm. Figure 6 shows the addition of Hg^{2+} metal ion in the concentration range of $5x10^{-7}$-$5x10^{-4}$ M has an increase in fluorescence intensity (turn-on), i.e. the lighting effect increases the increase of metal concentration.

The magnetic properties of a metal affect fluorescence intensity. The Hg^{2+} ion is a diamagnetic metal that tends to increase fluorescence intensity. Figure 6 shows that with the addition of Hg^{2+} in the concentration of $5x10^{-7}$ M, a significant decrease occurs in emission fluorescence intensity. Electrons in the excited energy level return to the ground state at the time of emission by releasing less energy in the form of fluorescence (radiation emission) than electrons that experience non-radiant emission. Most likely, this is due to the small number of Hg^{2+} ions contained in the complex, but as the concentration of Hg^{2+} ions increases, the emission intensity continues to increase [15].

6. Study of Complex Compound Fluorescence with the Addition of Cu^{2+} Metal Ion

The addition of Cu^{2+} metal ion is carried out at the concentration of $5x10^{-7}$-$5x10^{-4}$ M into a complex compound with the concentration of $5x10^{-5}$ M in methanol-chloroform solvent (1:1).

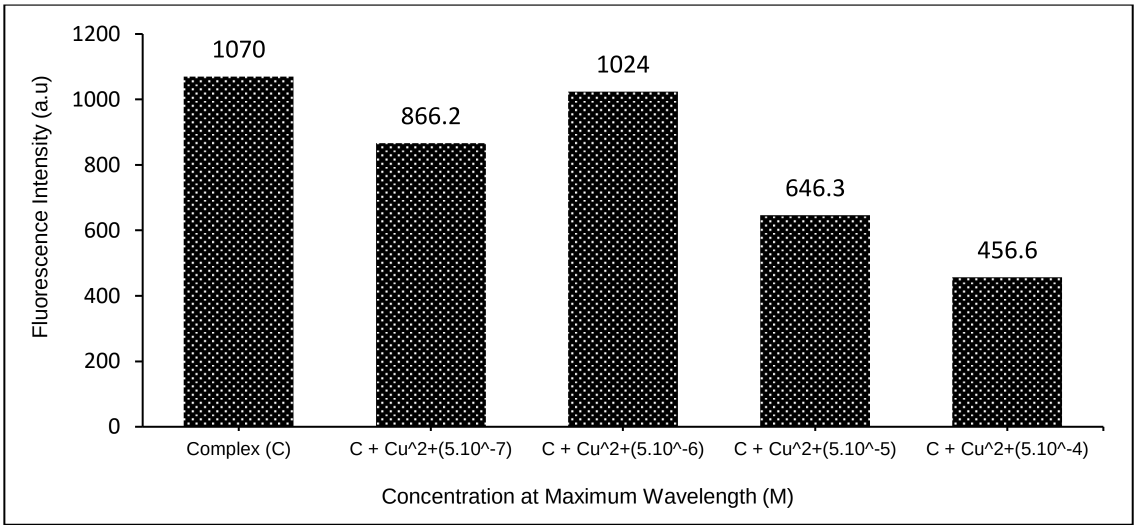

Figure 7. Chart on change in the fluorescence intensity of complex compounds against the addition of Cu^{2+} heavy metal ion at various concentrations.

Figure 7 shows that, with the addition of Cu^{2+} ion, there is an increase followed by a decrease in fluorescence intensity (turn on-off). The fluorescence quenching (turn-off) mechanism is the result of the quencher interaction when electron excitation occurs. Extinguishing agents can be heavy metals or paramagnetic elements. The Cu^{2+} ion is a paramagnetic metal [16]. Paramagnetic elements have unpaired electrons in the d orbitals, causing a change of electrons in the compound's excited orbitals, resulting in a triplet excited state. This phenomenon is known as an inter-system crossing. The process of returning electrons in triplet excitation to the ground state is prohibited, so it runs slowly [15].

A shift or change in light intensity and cell position can cause measurement errors. This effect, known as the inner filter caused by the difference in phosphorescence and fluorescence intensity on the right and the cuvette on the left, can also create errors in measurement [17]. Thus, it can be said that when the Cu^{2+} ion at the concentration of $5x10^{-6}$ M is added, there is an increase in emission fluorescence intensity due to the inner filter effect.

Based on the results of the fluorosensor study, the determination of the type of fluorosensor of the metal ion complex compound Co^{2+} and the para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand can be influenced by the magnetic properties of the metal ion it binds.

CONCLUSION

The complex compound of Co^{2+} metal ion and para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand is successfully synthesized and obtained with the yield of 36% and the melting point of 243.2°C. Characterization by FTIR (KBr, cm^{-1}) generates: 3060.65 (C-H aromatic); 2919.46-2851 (C-H pyridine); 2363.23 and 1640.14 (C=N); 1594.5-1493.24 (C=C aromatic) and 1326.38-1019.74 (C-N). The

The result of fluorescence intensity is 1150 a.u. At the wavelength of 470 nm and the molar absorptivity value of log ε 4.23 at the wavelength of 366 nm and log ε 4.44 at the wavelength of 250 nm. The result of the fluorosensor study shows that the complex compound of Co^{2+} metal ion and para-di-2-(1-phenyl-3-pyridyl-4,5-dihydro-1H-pyrazole-5-yl)benzene ligand has the potential to be used as a fluorosensor for Hg^{2+} heavy metal ion with "turn-on" type and Cu^{2+} heavy metal ion with "turn on-off" type.

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REFERENCES

[1] N. Cahyani, D. T. F, Lumban Batu, & S. Sulistiono., "Kandungan Logam Berat Pb, Hg, Cd, Dan Cu Pada Daging Ikan Rejung (Sillago Sihama) Di Estuari Sungai Donan, Cilacap, Jawa Tengah," JPHPI,vol.19,no.3, pp.267-276, 2016. doi: 10.17844/jphpi.v19i3.15090.

[2] M. M. Li, W. B. Zhao, T. T. Zhang, W. L. Fan, Y. Xu, Y. Xiao, J. Y. Miao, & B. X. Zhao., "A New Thiophenyl Pyrazoline Fluorescent Probe for Cu2+ in Aqueous Solution and Imaging in Live Cell," *J Fluorese*,vol. 6 no. 1, 1-7, 2013. doi: 10.1007/s10895-013-1259-x.

[3] W. C. Lin, C. Y. Wu, Z. H. Liu, C. Y. Lin, & Y. P. Yen., "A new selective colorimetric and fluorescent sensor for Hg2+ and Cu2+ based on a thiourea featuring a pyrene unit," *Talanta*, vol. 81, pp. 1209-1215, 2010. doi: 10.1016/j.talanta.2010.02.012.

[4] Rosihan & Husaini, "Logam Berat Sekitar Manusia," Lambung Mangkurat University Press: Banjarmasin, 2017. ISBN: 978-602-6483-47-8.

[5] S. H. J. Sari, J. F. A. Kirana, & Guntur., "Analisis Kandungan Logam Berat Hg

dan Cu Terlarut di Perairan Pesisir Wonorejo, Pantai Timur Surabaya," *Jurnal Pendidikan Geografi*. vol. 22, no. 1, pp 1-9, 2017.
doi: 10.17977/jpg.v22i1.375.

[6] Ciupa, M. F, Mahon, P. A. De Bank, & L. Caggiano., "Simple pyrazoline and pyrazole "turn on" fluorescent sensors selective for Cd2+ and Zn2+ in MeCN," *Organic & Biomolecular Chemistry*, 10 (44), 8753-8757, 2012.
doi:10.1039/C2OB26608C.

[7] S. Hu, S. Zhang, Y. Hu, Q. Tao, & A. Wu., "A new selective pyrazoline-based fluorescent chemosensor for Cu2+ in aqueous solution," *Dyes and Pigments*. vol. 96: 509-515, 2013. doi: 10.1016/j.dyepig.2012.09.019.

[8] Y. Saria, L. Lucyanti, N. Hidayati, & A. Lesbani, "Sintesis Senyawa Kompleks Kobalt dengan Asetilasetonato," *Jurnal Penelitian Sains*, vol.15, no.3, pp. 115-117, 2012.
doi: 10.26554/jps.v15i3.107.

[9] G. Yang, X. Meng, S. Fang, H. Duan, L. Wang, & Z. Wang., "A highly selective colorimetric fluorescent probe for detection of Hg2+ and its application on test strips," *RCS Advances*. vol. 9, no 15, pp. 8529-8536, 2019.
doi: 10.1039/C9RA00797K.

[10] E. S. Hermawati, Suhartana, & Taslimah., "Sintesis dan Karak-terisasi senyawa kompleks Zn(II)-8-Hidroksikuinolin," *Jurnal Kimia Sains dan Aplikasi.* Vol.19, no3, pp. 94-98, 2016.
doi: 10.14710/jksa.19.3.94-98.

[11] J. V. Mehta, S. B. Gajera, & M. N. Patel., "Design, synthesis and biological evaluation of pyrazoline nucleus based homoleptic Ru(III) compounds," *Patel, Med. Chem. Commun*. vol.7, no. 7, pp1-3, 2016.
doi: 10.1039/C6MD00149A.

[12] A. N. Kharat, A. Bakhoda, G. Bruno, & A. H. Rudbari., "Urease inhibitory activities of ZnBr2 and ZnI2 complexes of terpyridine derivatives: Systematic investigation of aryl substituents on urease inhibitory activities," *Polyhedron*, vol. 45, pp. 9-14, 2012.
doi: 10.1016/j.poly.2012.07.035.

[13] D. L. Pavia, G. Lampman, & G. Kriz., "Introduction To Spectroscopy," Third Edition. Thomson Learning: Singapura, 2001.
ISBN:9780495555759.

[14] Y. Z. Hakim & A. Zulys, "A Fluorescence Study of Pyrazole Derivative 2-(1,5-diphenyl-4,5-dihydro-1H-pyrazole-3-yl)pyridine Upon Addition of La3+ and Eu3+ Ions," International Conference on Materials, Manufacturing and Mechanical Engineering, pp. 362–366, 2016.
doi: 10.12783/dtmse/mmme2016/10140.

[15] J. R. Lacowicz, "Principle of Fluorescence Spectroscopy," University of Maryland School of Medicine Baltimore, Maryland, USA (3rd Ed), 2006.
doi: 10.1007/978-0-387-46312-4.

[16] B. Malau & A. Zulys. "Ligand 4'-(4-carboxyphenyl)-2,2':6',2"-terpyridine Grafted With TiO2–Complexation With The Ions Metal Transition And Application As Fluorosensor For Na+ Ion," IOP. Vol..18,pp.. 1-9, 2017.
doi: 10.1088/1757-899X/188/1/012044.

[17] P. Ding, X. Xin, L. Zhao, Z. Cie, Q. Zhang, J. Jiao, & G. Xu., "On–off–on fluorescent oligomer as a chemosensor for the detection of manganese(VII), sulfur(II) and aldehydes based on the inner filter effect," RSC Advances. vol.7, no.6, pp. 3051-3058, 2017.
doi: 10.1039/C6RA25583C.