SOLVENT EFFECT ON THE COMPLEX TRIS(1,10-PHENANTROLINE)IRON(III) TRINITRATEHYDRATE FORMATION AS MAGNETIC MATERIAL

[1]AYU FAHIMAH DINIYAH WATHI, [2]BAMBANG RUSDIARSO, [3]NURYONO

[1,2,3]Department of Chemistry, Universitas Gadjah Mada, Special Region of Yogyakarta, Indonesia
E-mail: [1]ayufahimahdw@gmail.com, [2]bambangrusdiarso@gmail.com, [3]nuryono_mipa@ugm.ac.id

Abstract - The synthesis and structure of complex compound-based 1,10-phenantroline and Fe(III) have been synthesized and fully characterized. This study focuses on the use of different solvents. Synthesis process was conducted by adding 1,10-phenantroline to Fe(NO3)3•9H2O in methanol (complex 1) and ethanol (complex 2) to know the effect on the structure that was formed. Analysis of complex compound is done by several instrumens. FTIR spectrophotometer revealed absorption band of 1,10-phenantroline, nitrate ion, and coordination bond between Fe and N of 1,10-phenantroline. Refinement of XRD spectra towards tris(1,10-phenantroline)Iron(III) trinitrate monohydrate shows the similar structure between complexes and tris(1,10-phenantroline)Iron(III) trinitrate monohydrate. Analysis by magnetic susceptibility balance (MSB) indicate that complex compounds are paramagnetic at room temperature. Analysis by AAS reveals that complex 1 formed [Fe(phenantroline)3](NO3)3•10H2O while complex 2 formed [Fe(phenantroline)3](NO3)3•9H2O.

Keywords - Complex, Fe(III), 1,10-Phenantroline, Paramagnetic

I. INTRODUCTION

Iron (III) is reactive that can form many compounds with various ligands [1]. Initially a complex compound is known as a coordinating compound. In complex compounds, the central or ion atom is coordinated by one or more molecules or ions (ligands) acting as Lewis bases forming a coordination bond. Central or ionic atoms in complex compounds act as Lewis acids. Atoms in a ligand that act as an atomic donor are bonded directly to a central or ion atom. Lewis base donates electron pairs to Lewis acid to form coordination bonds and produces adductor species [2].
In 1893, Alfred Werner proposed a theory to explain the existence of complex compounds such as $CoCl_3 \cdot 6NH_3$, $CoCl \cdot 4NH_3$, $PtCl_2 \cdot 2NH_3$, and $Fe(CN)_3 \cdot 3KCN$. Alfred Werner begins by assuming that metal ions have two kinds of valence, the primary valence and the second valence[3].

The complex compounds were first discovered by Alfred Werner used as pigments and dyes since ancient times. Examples of the coordination compound used were Prussian blue ($KFe[Fe(CN)_6]$), aureolin ($K_3[Co(NO_2)_6] \cdot 6H_2O$), and aalizarin red dye (calcium aluminum salt of 1,2-dihydroxy-9,10-anthraquinone). The formula of these compounds was concluded at the end of the nineteenth century which provides a background in the development of bond theory [4].
Complex compounds have many benefits in life and can also be used as catalysts, dyestuffs, and magnetic materials as well. Magnetic material is used in various applications in life that is in the manufacture of electrical objects. Magnetic materials are used for data storage on audio, video, computer disk, cassette recorder, and electric pump [5]. Magnetic material is used for the body scanning process by MRI. Various tools in the household also use a lot of materials such as CD players, television, and loudspeakers. Genetic material becomes very important in the development of modern society. The need for efficient use in the development of magnetic material design [6].

In 2004, Odoko and Okabe succeeded in synthesizing tris(1,10-phenantroline-κ2N,N')iron(III)trinitrate mono- hydrate complex. Synthesis was carried out by mixing Fe $(NO_3)_3 \cdot 9H_2O$, 1,10-phenantroline and malonic acid with 1: 1: 1 molar ratio using DMF solvent. Prismatic brown crystalis obtained at room temperature by slow evaporation. The structure of the compound has been confirmed by characterization using X-ray crystallography. Fe atomis located on the double-axis of rotation and are coordinated by three planar lions of 1'10-fenantroline in octahedral structures with slight distortion. One anion nitrate and one water molecule are tied to the double rotation axis. Structure of tris(1,10-phenantroline-κ2N,N') iron(III)trinitrate mono- hydrate complex as in the following figure [7]:

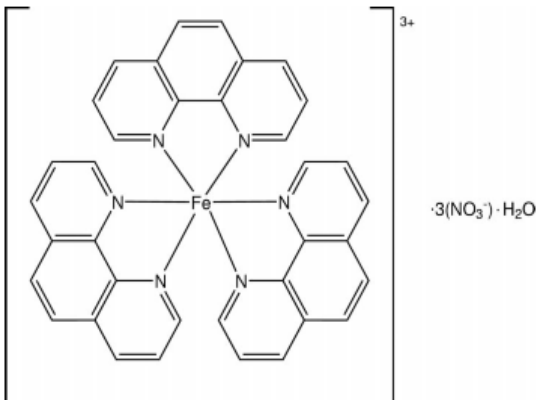


Fig.1..Structure of tris complex compounds (1,10-phenantroline-κ2N,N')iron(III)trinitrate monohydrate [7]

Joris and Male reported a study on the synthesis of single core complex [Fe(phenantroline)$_2$(NCS)$_2$]. The synthesis was performed by using a ligand 1,10-phenantroline and NCS ions in a water solvent using direct method, reflux, and slow diffusion. All three products are paramagnetic complex compounds with magnetic moment of 4.841 BM, 5.037 BM, and 4.989 BM respectively [8]. Based on the description among magnetic materials in various applications, it is necessary to synthesis the magnetic material from iron(III).

III. DETAILS EXPERIMENTAL

2.1 Materials and Instrumentation

All reagents were from commercial sources. Iron(III) nitrate nonahidrate ($Fe(NO_3)_3 \cdot 9H_2O$), 1,10-phenantroline ($C_{12}H_8N_2$), methanol (CH_3OH), ethanol (C_2H_5OH), and diethylether ($C_4H_{10}O$) were purchased from Merck. Instrumentations that were used are Fourier Transform Infrared Shimadzu Prestige-21, UV-Vis Shimadzu 1700 spectrophotometer, XRD Rigaku spectrophotometer, Magnetic Susceptibility Balance Sherwood Scientific, and Atomic Absorption Spectroscopy Analytik Jena contAA 300.

2.2 Synthesis of Fe (III) Compound-Ligand 1,10-phenantroline with Methanol (1)

0.404 g of $Fe(NO_3)_3 \cdot 9H_2O$ dissolved with methanol until dissolved. In another glass, 0.3 g of 1,10-fenantroline ligand are dissolved with methanol. Both are mixed and stirred in the sonicator for an hour. The glass is covered with filter paper and left for several days until all the solvent evaporate slowly and form solids. The synthetic solid is washed with diethylether. Characterization of complex compounds of synthesis was analyzed using FTIR, UV-Vis, XRD, MSB, and AAS

2.2 Synthesis of Compound Fe(III)-Ligand 1,10-phenantroline with Ethanol (2)

0.404 g of $Fe(NO_3)_3 \cdot 9H_2O$ coupled with ethanol until dissolved. In another glass, 0.3 g of 1,10-fenantroline ligand are dissolved with ethanol. Both are mixed and stirred in the sonicator for an hour. The glass is covered with filter paper and left for several days until all the solvent evaporate slowly and form solids. The synthetic solid is washed with diethylether. Characterization of complex compounds of synthesis was analyzed using FTIR, UV-Vis, XRD, MSB and AAS.

III. RESULTS AND DISCUSSION

3.1 Physical properties of complex compound

Compounds of iron complex III with 1,10-phenantoline ligand are synthesized by the addition of 1,10-phenantoline ligand to $Fe(NO_3)_3 \cdot 9H_2O$ using methanol and ethanol solvent because they have volatile properties to obtain solid by slow evaporation. The reaction of forming complex compounds with 1,10-phenantoline ligand can be written as follows:

$$Fe(NO_3)_3 \cdot 9H_2O + 3C_{12}H_8N_2 \rightarrow [Fe(C_{12}H_8N_2)_3](NO_3)_3 \cdot xH_2O$$

Complex compound obtained is weighed and is seen their physical properties. Physical properties of complex compounds are shown in Table 1.

Table 1. Physical properties of complex compound

Complex	Weight (mg)	Color
1	376.7	Red
2	323.4	Red

3.2 FTIR analysis

FTIR spectra of complex 1 provides an absorption band of OH bonds at wavenumber 3371,57 cm^{-1}, an absorption band of NO_3^- ion at wavenumber 1381,03 cm^{-1},an absorption band Fe-N bond at wavenumber 362,62 cm^{-1}, an aromatic ring CH band absorber at wavenumber 3055,25 cm^{-1}, C = N band at wavenumber 2337,72 cm^{-1}, and C = C aromatic absorption band at wavenumber 1512,19 cm^{-1}[9][10]. **Fig. 2**shows that complex 1 is successfully formed by the presence of Fe-N bond.

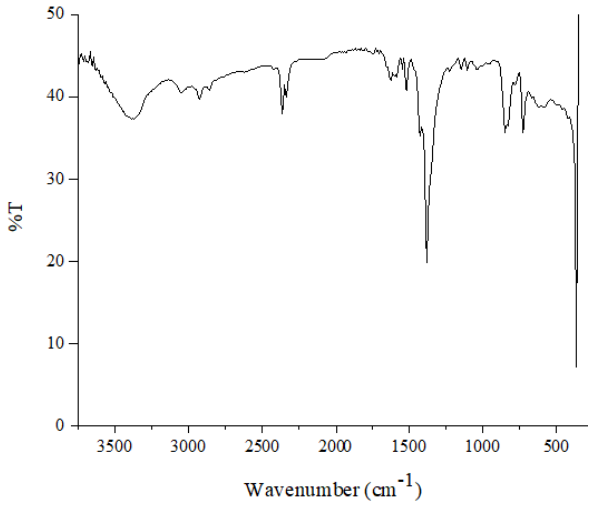


Fig. 2. FTIR spectra of complex 1

Complex **2**spectra reveals an OH bond at wavenumber of 3410.15 cm^{-1} and is supported by absorption bands at a wavenumber of 1627.92 cm^{-1} confirming that H_2O in a complex compound is bound as crystalline water, an ion-absorbing band NO_3^- wave band 1381,03 cm^{-1} and 1581,63 cm^{-1}, absorption band Fe-N bond at wavenumber 331,76 cm^{-1}, absorption band CH aromatic ring at wavenumber 3055,24 cm^{-1}, C = N bands of wavenumber 2337,72 cm^{-1}, and C = C aromatic absorption band at wavenumbers 1512,19 cm^{-1}[9][10]. **Fig. 3** shows that complex **2** is successfully formed by the presence of Fe-N bond.

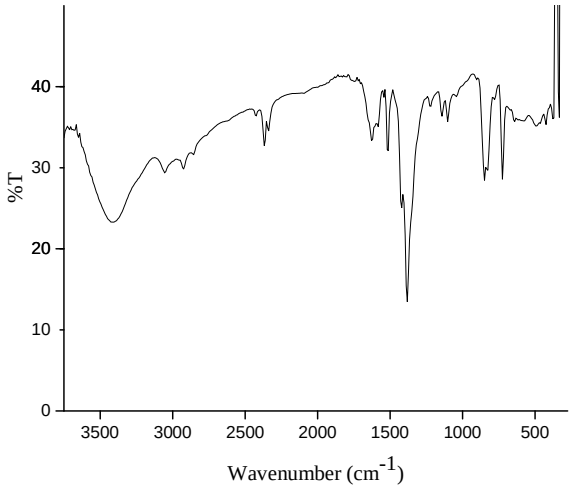


Fig. 3.FTIR spectra of complex 2

3.3 UV-Vis analysis

The complex compounds were characterized using UV-Vis spectrophotometer. Analysis using the UV-Vis spectrophotometer is presented in Fig.4 and Fig. 5.Fig. 4 shows that the compound **1**and **2**have a maximum wavelength (λmax) of 266 nm. Fig. 5shows that $Fe(NO_3)_3 \cdot 9H_2O$ compound have λmax at 264 nm. Based on comparison of λmaks of complex compounds of synthesis with λmaks compound $Fe(NO_3)_3 \cdot 9H_2O$, then it can be concluded that iron in complex **1** and **2** is Fe(III).

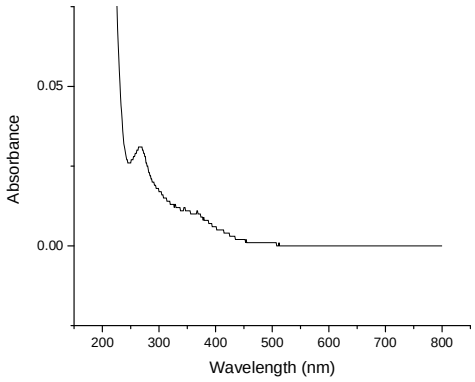


Fig. 4. UV-Vis spectra of $Fe(NO_3)_3 \cdot 9H_2O$

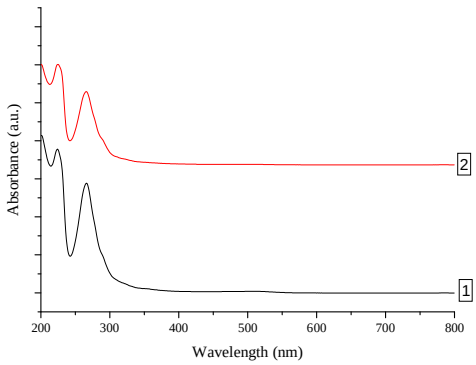


Fig. 5. UV-Vis spectra of complex 1 and 2

3.4 XRD analysis

Structure analysis of complex compounds was performed using XRD spectrophotometer. The determination of the structure of complex compounds is determined by comparing the parameters of crystalline properties to crystals of similarity to the formula. The comparison was performed using the Le Bail method of the Rietica program, which found that XRD spectra of complex compound with 1,10-phenantroline ligand were similar to the crystallography data of the complex $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$. Comparison of XRD spectra of the synthesis results with crystallography dataof $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$ based on research reported by Odoko and Okabe (2014)is shown in Table 2and Table 3.

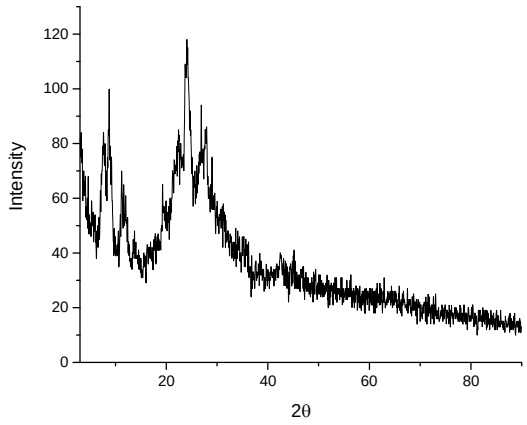


Fig. 6. XRD spectra of complex 1

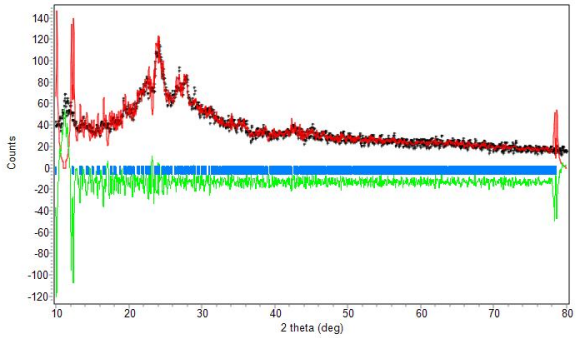


Fig. 6. Refinement of complex 1 to complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$

Table 2. Refinement of complex 1 to complex compounds $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$

Parameter	$[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$	Complex 1
Crystal System	Monoclinic	Monoclinic
Space Group	C2/c	C2/c
a (Å)	10.781	10.912
b (Å)	24.53	24,96
c (Å)	13.286	13.72
α (˚)	90	90
β (˚)	103.15	103.56
γ (˚)	90	90

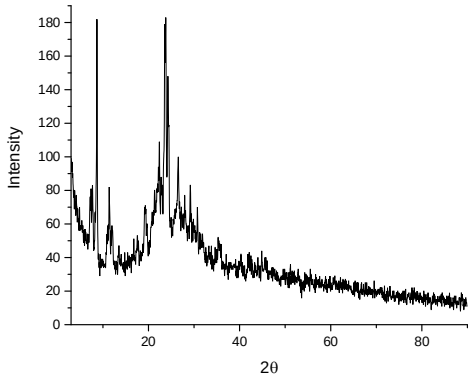


Fig. 7.XRD spectra of complex 2

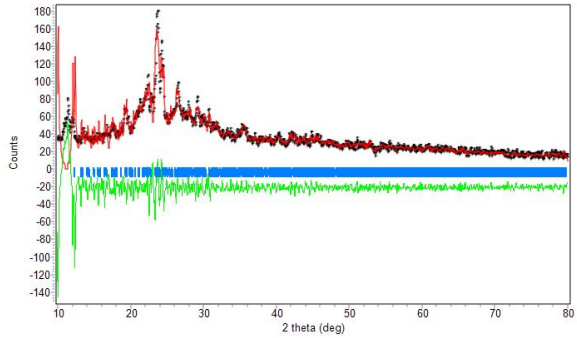


Fig. 8. Refinement of complex compound 2 to complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$

Table3. Refinement of complex compound 8 to complex compounds $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$

Parameter	$[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$	Complex **2**
Crystal system	Monoclinic	Monoclinic
Space Group	C2/c	C2/c
a (Å)	10.781	10.96
b (Å)	24.53	25.22
c (Å)	13.286	13.81
α (˚)	90	90
β (˚)	103.15	103.7
γ (˚)	90	90

Complex **1** has a similar structure that is octahedral with complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$. Compound **1** has a monoclinic crystal system with space group C2/c, the value of a, b, c are 10.912; 24.96; 13.72 Å, and the value of α, β, γ are 90, 103.56, 90˚. Complex **2** also has similar structures with complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot H_2O$ as indicated by the little difference in parameters. Complex **2** has a monoclinic crystal system with space group C2/c. The value of a, b, c are 10.96; 25,22; 13.81 Å while the value of α, β, γ is 90; 103,7; 90˚.

3.5 MSB analysis

The synthesis of complex compounds were performed using a bidentate nitrogen ligand of 1,10-phenantroline. The 1,10-fenantrolin ligand has two N atoms that can donate two pairs of electron to the central atom resulting in complexes with chelat[4].

Table 4. Magnetic moment of complex compound

Complex	Magnetic Moment (BM)
1	1,5
2	1,4

1,10-fenantroline ligand is strong ligand (Miessler, 2014) so that the arrangement of electrons in the d orbitals within Fe atoms tends to fill the t_{2g} orbital first. The electron filling in the t_{2g} orbital first is due to large Δ_o due to the strong ligand. Ion Fe(III) in a complex compound in a low spin state. All complex compounds that are formed have red color and magnetic moment value in the range of 1.4 to 1.5 BM. Magnetic moment in the range of 1,4-1,5 BM proves that iron ion in complex compound is Fe(III) that have one unpaired electron.

3.6 AAS analysis

The percentage of iron in compound **1** is known to be 5.283% by AAS so it is close to the theoretical iron percentage for $[Fe(phenantroline)_3](NO_3)_3 \cdot 10H_2O$. Compound complex **2** has 5.44% iron which approximates the theoretical percentage of iron to complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot 9H_2O$.

Complex **1** used methanol as solvent and complex **2** used ethanol as solvent. Complex 1 have more H_2O in crystal of complex compound that is caused by boiling point of ethanol is greater than methanol. Methanol has boiling point at 65 ˚C, while ethanol has boiling point at 65 ˚C. Methanol evaporate faster than ethanol so it is not strong to attract H_2O from crystal compared with ethanol.

Table 5. %iron in complex compound theoretically
*x=$[Fe(phenantroline)_3](NO_3)_3$

No.	Formula	Relative mass of complex (g/mol)	%Fe (%)
1	x	782,49458	7,13
2	$x \cdot H_2O$	800,5	6,9
3	$x \cdot 2H_2O$	818,52	6,82
4	$x \cdot 3H_2O$	836,54	6,67
5	$x \cdot 4H_2O$	854,55	6,5
6	$x \cdot 5H_2O$	872,57	6,4
7	$x \cdot 6H_2O$	890,58	6,27
8	$x \cdot 7H_2O$	908,6	6,14
9	$x \cdot 8H_2O$	926,6	6,02
10	$x \cdot 9H_2O$	944,63	5,9
11	$x \cdot 10H_2O$	962,64	5,8

Table6. Formula of complex compound

Complex	Formula
1	$[Fe(phenantroline)_3](NO_3)_3 \cdot 10H_2O$
2	$[Fe(phenantroline)_3](NO_3)_3 \cdot 9H_2O$

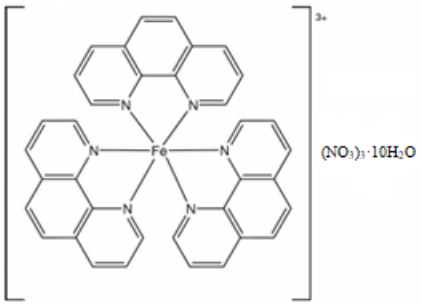


Fig. 9. Approximate structure of complex 2

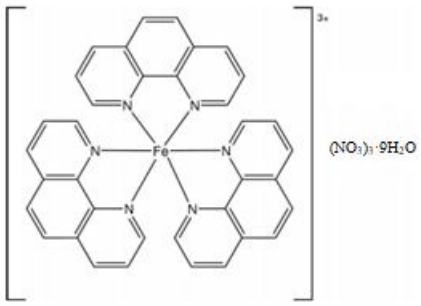


Fig. 9. Approximate structure of complex 2

CONCLUSION

Complex compound $[Fe(phenantroline)_3](NO_3)_3 \cdot xH_2O$ was successfully synthesized. It was shown by the analysis of UV-Vis, FTIR, and XRD. Complex compound 1 and 2 are obtained 376.7 and 323.4 mg. Both are in red colour. Complex 1 and 2 have same structure that is octahedaral but have different number of H_2O. Complex 1 with methanol as solvent have more H_2O than complex 2 with ethanol as solvent that is caused by boiling point of ethanol is greater than methanol. Complex compound 1 and 2 was analysed by MSB and was known that both are paramagnetic which has the potential to become magnetic material.

ACKNOWLEDGEMENTS

This investigation was supported by Indonesia Endowment Fund (LPDP) and Laboratory of Inorganic Chemistry of UniversitasGadjahMada

REFERENCES

[1] C. F.A. Wilkinson G. and P. L. Gauss, Inorganic Chemistry 3rd Edition, John Willey & Sons Inc. New York, 1995, Housecroft and Sharpe, Inorganic Chemistry, Pearson, London, 2005
[2] J. E. House, Inorganic Chemistry, Elsevier, London, 2008
[3] G. L. Miessler, P. J. Fischer, D. A. Tarr, Inorganic Chemistry, Pearson, New York, 2014
[4] J.M.D. Coey, Magnetism and Magnetic Materials, Cambridge University Press, New York, 2009
[5] I.R. Harris and A.J. Williams, Magnetic Materials, Material Science and Engineering, Vol. II, 2009
[6] S. Attia, S. Bhattacharya, C. G. Pierpont, Potential for Redox Isomerism by Quinone Complexes of Iron(III). Studies on Complexes of the FeIII(N-N)(DBSQ)(DBCat) Series with 2,2'-Bipyridine and N,N,N',N'-TetramethylethylenediamineColigands, Inorganic Chemistry, Vol. 34, 4427-4433, 1995
[7] X. Wang and D. M. Stanbury, Oxidation of Iodide by a Series of Fe(III) Complexes in Acetonitrile, Inorganic Chemistry, Vol. 45, 3415-3423, 2006
[8] M. Odoko and N. Okabe, Tris(1,10-phenantroline-κ2N,N')iron(III) Trinitrate Monohydrate, ActaCrystallographica Section E, Vol. 60, 1822-1824, 2004
[9] Joris and Male, 2011, MetodeInovatifTermodifikasiuntukSintesisKompleks Inti Tunggal [Fe(fen)2(NCS)2], Seminar Nasional Kimia 2011
[10] D. L. Pavia, G. M. Lampman, G. S. Kriz, J. R. Vyvyan, Introduction to Spectroscopy, Cengage Learning, Washington, 2009
[11] Nakamoto, Kazuo, Infrared and Raman Spectra ofInorganic and Coordination Compounds, John Wiley & Sons, Inc., Canada, 2009.

★★★