

Zn(II) COMPLEX OF 2,6-BIS(4-NITROBENZAMIDO)PYRIDINE:

SYNTHESIS AND CHARACTERIZATION

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ABSTRACT

Zn(II) complex containing pyridine and benzamide units was prepared via two step reactions. Nucleophilic chloro-displacement reaction of 2,6-diaminopyridine with 4-nitrobenzoyl chloride in the presence of propylene oxide afforded 2,6-bis(4-nitrobenzamido)pyridine (BNBP) as a ligand. This step reaction using Taremi method with some modifications and continued by refluxing method with $ZnCl_2$ to produced complex compound. Characterization of compound by 1H -NMR indicated that there are 5 types of protons, with each shift (δ) 10.893 s, (δ) 8.318 d, (δ) 8.174 d (δ) 7.896 t, and (δ) d 7.870 ppm. ^{13}C NMR spectra showed 8 types of carbons on each region shifts (δ) 160.135, (δ) 145.766, (δ) 144.917, (δ) 135.840, (δ) 135.421, (δ) 125.066, (δ) 119.088 and (δ) 107.466 ppm. Characterization of Zn(II) complex using the FTIR showed that the complex bond is formed from the free electron pair donated by N-H amide of 2,6-bis (4-nitrobenzamido) pyridine. UV-Vis spectra showed a maximum wavelength 320 nm of complex Zn(II), it shows the $\pi \rightarrow \pi^$ intraligand transition.*

keyword:

Zn(II), complex, synthesis, characterization

INTRODUCTION

Complex compounds continue to be developed into useful compounds for medical treatment. Several complex compounds have been successfully synthesized and show good activity in medicinal chemistry, especially in complex with organic compounds. It makes the research on the use of organic complexes need to be improved.

Complex compounds composed of metals and ligands. Some of non-platinum metals such as Zn(II), Co(II), Ni(II), Fe(II), and Fe(III) successfully used as a complex compound [1,2,3]. Zinc (Zn) is one of the most important trace elements in the body and it is essential as a catalytic, structural and regulatory ion. It is involved in homeostasis, in immune responses, in oxidative stress, in apoptosis and in ageing. Zn is also needed in the growth and development of microorganisms, whether plants, animals, and humans [4]. Zinc metal is transition metal of IIB group which has the atomic number 30 with $[\text{Ar}] 4s^2 3d^{10}$ electron configuration. Zn(II) metal cation providing a blank orbital which can be used to receive free electron pair from ligand. Therefore, Zn can be used as one of the candidate metals that can bind ligands well.

Complex activity of the metal ion is affected by ligand coordinated. Some of ligands are constantly being developed for drugs compounds are organic ligands such as pyridine [5,6], benzamide [7], and imidazole [8]. Ligands that have free electron pairs from nitrogen and oxygen atoms. Pyridine showed a biological activity as an antimicrobial, anti-inflammatory, analgesic [5] and anticancer [7]. Some of Zn(II) complex compounds that can bind with organic ligands such as pyridine, benzamide, and imidazole has proven ability as an antibacterial [9,10], antioxidant [8], anti-inflammatory, and anti-cancer agents [2,3].

Zn(II) metal ion as a complex compound based on pyridine and benzamide units has been widely reported. Zn(II) complex has been synthesized with Schiff base obtained through the condensation of 2-aminobenzamide with thiophene-2-carbaldehyde formed $\text{Zn}(\text{L})\text{X}_2$ and $\text{Zn}(\text{L}_2)\text{X}_2$. All complexes have tetrahedral geometry and have a bioactivity for cancer line [2]. Besides, Zn(II) based on the V-shaped ligand 2,6-bis(2-benzimidazolyl)pyridine formed a six-coordinate in the structure of $[\text{Zn}(\text{bbp})_2(\text{pic})_2]\cdot\text{DMF}$, and forming a distorted octahedron. This complex is stronger than Cd(II) complex for the binding affinity [8].

Organic compounds based on benzamide and pyridine such as 2,6-bis(4-nitrobenzamido)pyridine has been synthesized [11]. 2,6-bis(4-nitrobenzamido)pyridine analog with a compound that successfully synthesized by Zhang and Li [7] and shows a good activity as a anticancer. Therefore, the main purpose of this research is to study Zn(II) metal ion synthesis with 2,6-bis (4-nitrobenzamido) pyridine and characterization as complex compounds. The structure which may be formed between ligand and Zn(II) complex compound will be studied using ^1H -NMR, ^{13}C -NMR, FTIR spectroscopy, and UV-Visible spectroscopy.

EXPERIMENTAL

Material and Method

All the chemical were used of p.a reagent from sigma aldrich and Merck. Metal salt ZnCl_2 , 2,6 diamino pyridine, *N,N*-methyl pirolidone, 4-nitrobenzoil chloride, propilen oxide, asetonitril p.a, Methanol, ethanol, Dimethyl formamide (DMF), and Dimethyl sulphoxide (DMSO).

Instrumen

Infrared measurements were performed on a SHIMADZU FTIR 8400S spectrophotometry. The ^1H NMR and ^{13}C NMR spectra were recorderd in dimethyl sulphoxide (DMSO- d_6) solution using JEOL RESONANCE, UV Visible Genesys 10S.

Synthesis of ligand

2,6-Bis(4-nitrobenzamido)pyridine ligand (BNBP) was prepared using method [11] with some modifications. A 250 mL two-necked round bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube and calcium chloride drying tube was charged with 2,6-diaminopyridine (0.015 mol) and NMP (90 mL). The mixture was stirred at 0°C for 30 minutes. Then, propylene oxide (about 43 mL) and 4-nitrobenzoyl chloride (0.09 mol, 13.635 g) were added and the mixture was stirred at 0°C for 30 minutes. The temperature was raised to room temperature (keep under 24°C temperature) and the solution was stirred for 22 h. 2,6-Bis(4-nitrobenzamido)pyridine was precipitated by pouring the flask content into water.

Then, it was filtered, washed with hot water and methanol successively and dried overnight under vacuum at 70°C (yield = 84,54%).

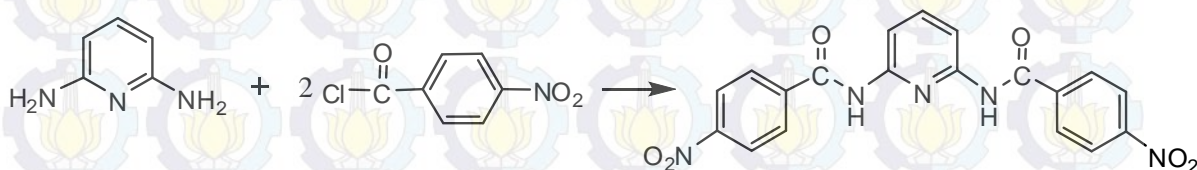


Fig. 1 Synthesis of the ligand L

Synthesis of metal complex

Solid ZnCl_2 (0.25 mmol) was added to a solution of methanol (10 ml). It was heated gently with stirring under reflux while BNPB (0.25 mmol in 1:1 methanol:acetonitrile solvents) was added. The mixture was heated under reflux 70°C for 24 h. it was aging at room temperature in the desiccators for 7 days to obtained a yellow brown solids.

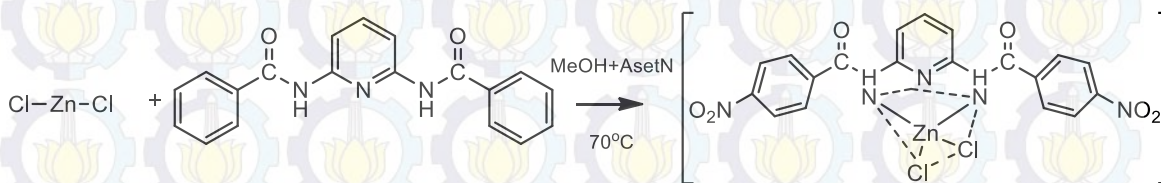


Fig. 2 The suggested synthesis of the metal complex

FTIR (Fourier-Transform Infrared) Spectrophotometer

This analysis used a Shimadzu FTIR 8400. A total of 1 mg of the sample was mixed with 10 mg of KBr, then put in a press holder, pressed to be thin and transparent pellets (0.01 mm - 0.05 mm). The sample holder is placed on the surface, inserted into a compartment and then observed the infrared spectrum.

RESULTS AND DISCUSSION

BNBP ligand was prepared by refluxing in N-methyl pyrrolidone (90 ml) an equimolar mixture of (0.03:0.09) 2,6-diamino pyridine and 4-nitrobenzoyl chloride. 2,6-bis(4-nitrobenzamido)pyridine ligand synthesized through the stages nucleophilic substitution reaction of 2,6-diaminopyridine with 4-nitrobenzoyl chloride in the presence of propylene oxide which acts as an acid scavenger. Ligands solids obtained greenish brown with a yield of 84.54%. The result of the melting point of

2,6-bis (4-nitrobenzamido)pyridine is 270-273°C this is in according with referent of 275-275°C [11]. The Structure of BNPB ligand was established by FTIR Spectrophotometry and ^1H -NMR (Table 1).

Table 1. FTIR Spectrophotometry and ^1H -NMR characterization of BNPB ligand

Substrate	IR (KBr, cm^{-1})	NMR (DMSO-d_6 , δ , ppm)	Melting Point ($^{\circ}\text{C}$)	Yield (%)
BNBP	3354.32	10.8935 s (2H, NH)	270-273	84.5
	1656.91	8.318 d (4H, phenyl)		
	1523.82	8.174 d (4 H, phenyl)		
	669.32	7.896 t (1H, pyridine)		
		7.870 d (2H, pyridine)		

^1H -NMR spectrum showed that 2,6-bis(4-nitrobenzamido)pyridine has been successfully synthesized. The following ^1H -NMR spectra of 2,6-bis(4-nitrobenzamido)pyridine synthesized (**Fig. 3**).

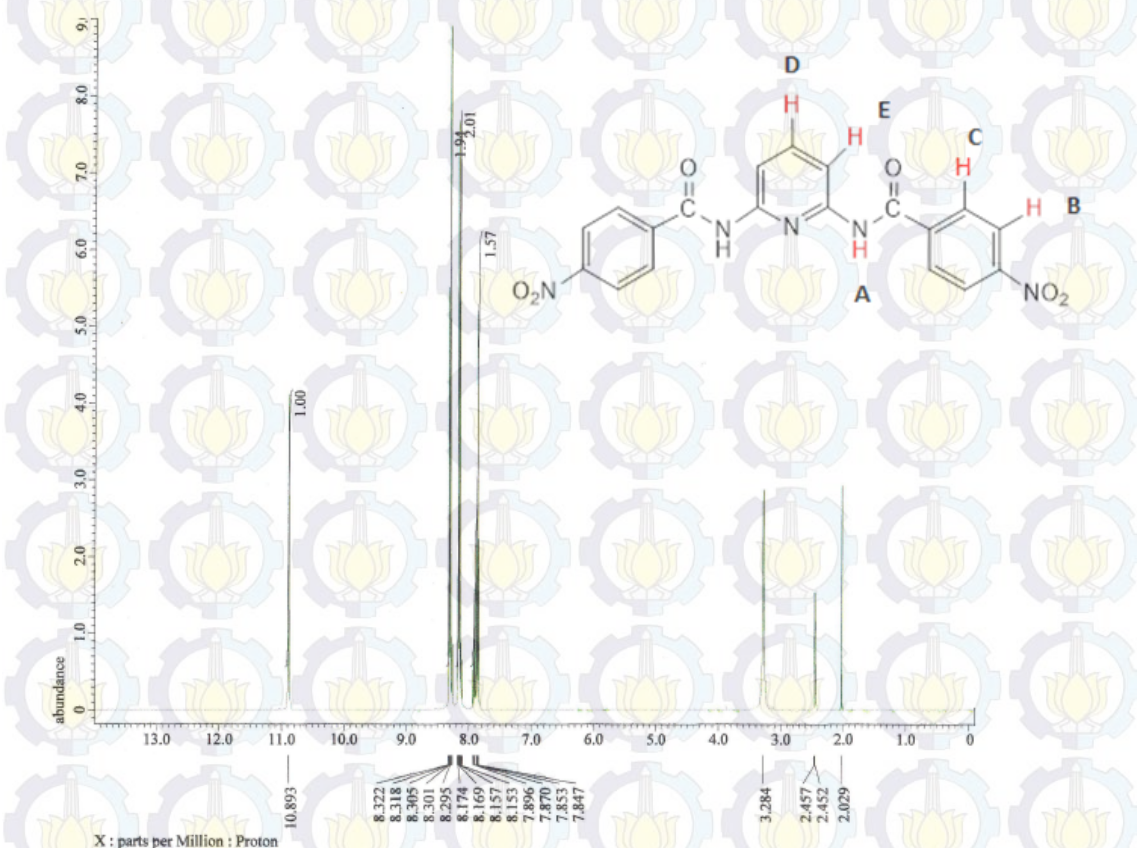


Fig. 3 ^1H -NMR spectrum of 2,6-bis(4-nitrobenzamido)pyridine

Based on the spectrum (**Fig.3**) shows there are 5 types of proton signals. Shifts (δ) 10.893 ppm show singlet NH peak with 2 protons, indicating that the protons do not have neighbors. Shifts (δ) 8.318 and 8.174 ppm doublet of proton

attached to the aromatic group, a proton in this area amounted into 8 protons. Triplet and doublet peaks of protons attached to the pyridine group shown in shifts (δ) 7.896 and 7.870 ppm with one proton and two protons respectively.

^{13}C -NMR spectrum (**Fig. 4**) showed that a shift (δ) 160,135 ppm of carbonyl group ($\text{C}=\text{O}$), shift (δ) 145,766 ppm and (δ) 144,917 ppm indicate the type of carbon near nitrogen atom. Type of carbon that is close to C atom shown in two shifts (δ) 135.840 and 135.421 ppm.

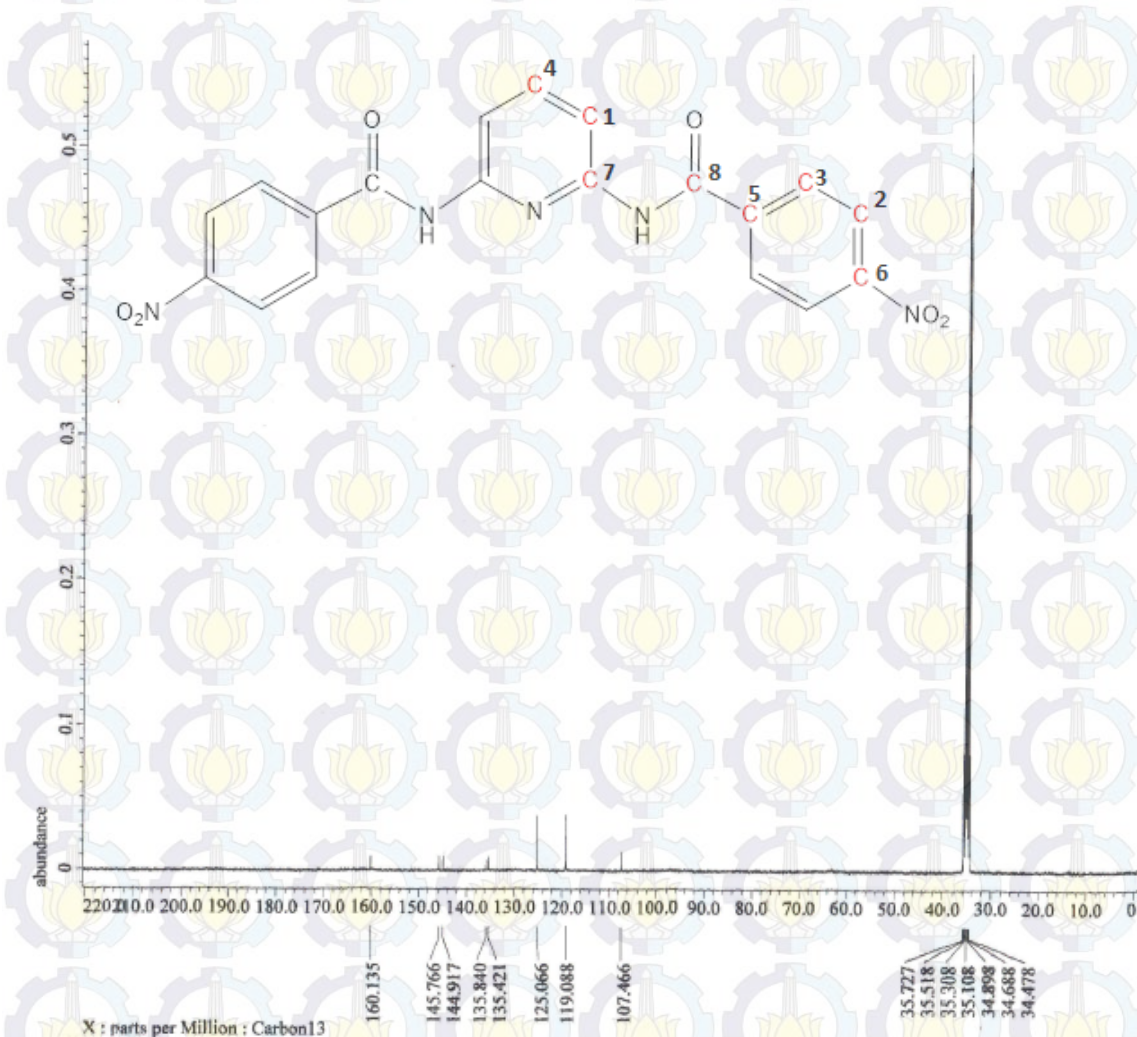


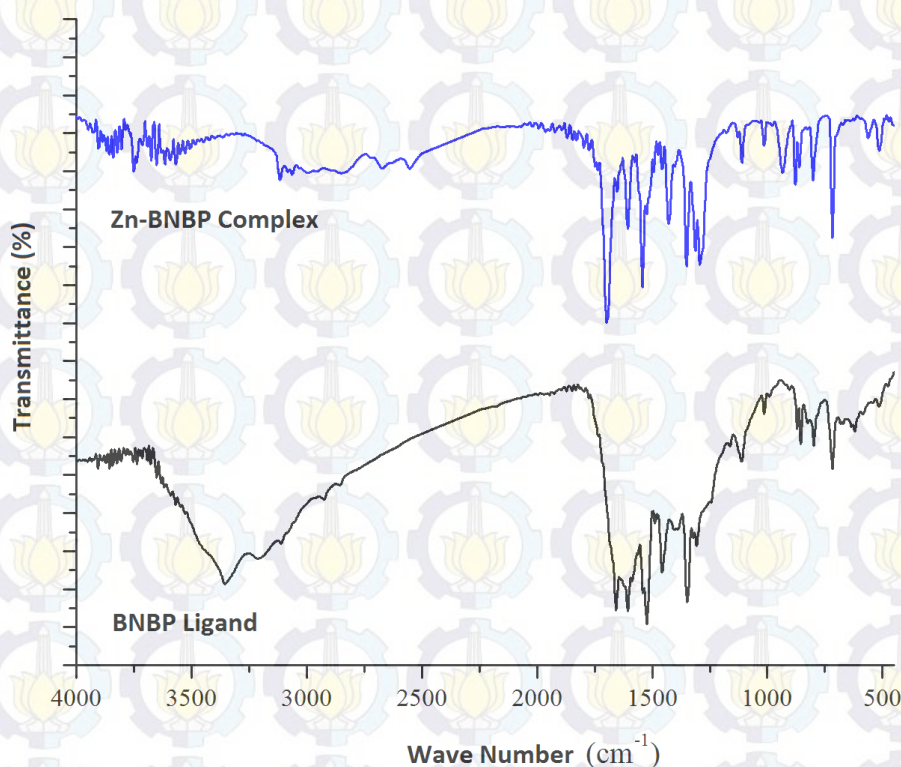
Fig. 4 ^{13}C -NMR spectrum of 2,6-bis(4-nitrobenzamido)pyridine

Shift values obtained from the data ^1H -NMR and ^{13}C -NMR is not much different from the previous Taremi [11] research results, so it can be ascertained that the compound 2,6-bis (4-nitrobenzamido) pyridine have been successfully synthesized. The summary of carbon types and shifts that occur in the compound 2,6-Bis (4-nitrobenzamido) pyridine are presented in Table 2.

Table 2. ^{13}C -NMR data of 2,6-bis(4-nitrobenzamido)pyridine

Carbon	Structure	δ_c (ppm)
C8	C of carbonyl (C=O)	160.135
C7	C=C of pyridine	145.766
C6	C=C of phenyl	144.917
C5	C=C of phenyl	135.840
C4	C=C of pyridine	135.421
C3	C=C of phenyl	125.066
C2	C=C of phenyl	119.088
C1	C=C of pyridine	107.466

Then, BNPB ligands that have been synthesized it complexed with Zn(II) metal ion, using the following metal salt ZnCl_2 formed $[\text{Zn}(\text{L})\text{Cl}_2]$ complex. The obtained complex are yellow brown crystalline solids which are stable in the air and decompose above 245°C .

**Fig. 5** FTIR Spectra of BNPB and Zn-BNPB complex

The IR spectra of synthesized ligand and complex (**Fig.5**) indicated the differences wave number for both ligand and complex. The wagging $\nu(\text{N-H})$ band for ligand is observable in the region 715.61 cm^{-1} of ligand and shift to 717.54 cm^{-1} of Zn(II) complex. This wavelength shift showed the band between nitrogen atom of

amide group with Zn(II). This data is supported by new band appeared at 563.23 cm^{-1} region which indicate the occurrence of N-Zn-N bonding on the complex. C=N Stretching 1604.83 cm^{-1} of pyridine no change of Zn(II) complex that indicates there is no band between nitrogen atom of pyridine at Zn(II) complex. So, the most likely form Zn(II) complex molecules proposed is $[\text{Zn}(\text{L})\text{Cl}_2]$ (**Fig. 6**).

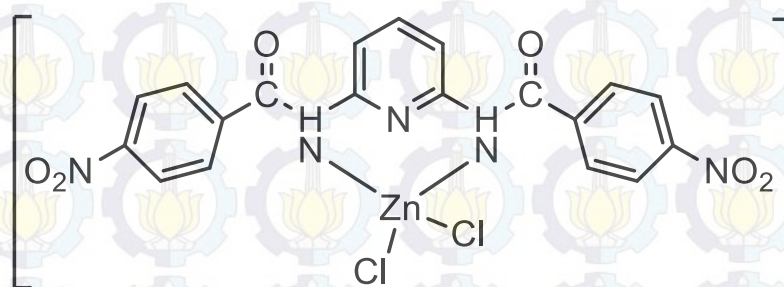


Fig. 6 Zn(II) complex molecules proposed

The UV-Visible spectra of Zn(II) complex in DMF were recorded at room temperature and the band positions of the absorption maxima (**Fig. 6**). For the studied Zn(II) complex the absorption spectra show a strong absorption band in UV region (230-320 nm). The maximum wavelength is 320 nm, that are probably assigned to the above mentioned intraligand transition. In addition, Zn(II) ion has $3d^{10}$ electron configuration therefore no $d \rightarrow d$ or LMCT band are feasible due to the completely filled d orbitals [12]. A $\pi \rightarrow \pi^*$ transition derived from unsaturated bond (aromatic) of 2,6-bis(4-nitrobenzamido)pyridine, these wavelength complex is derived from unsaturated bond (aromatic) of the ligand. These wavelength shift to hypsochromic of ligand at 250 nm to 260 nm. Based on these data it can be seen that the Zn(II) complex of BNBP ligand have been formed.

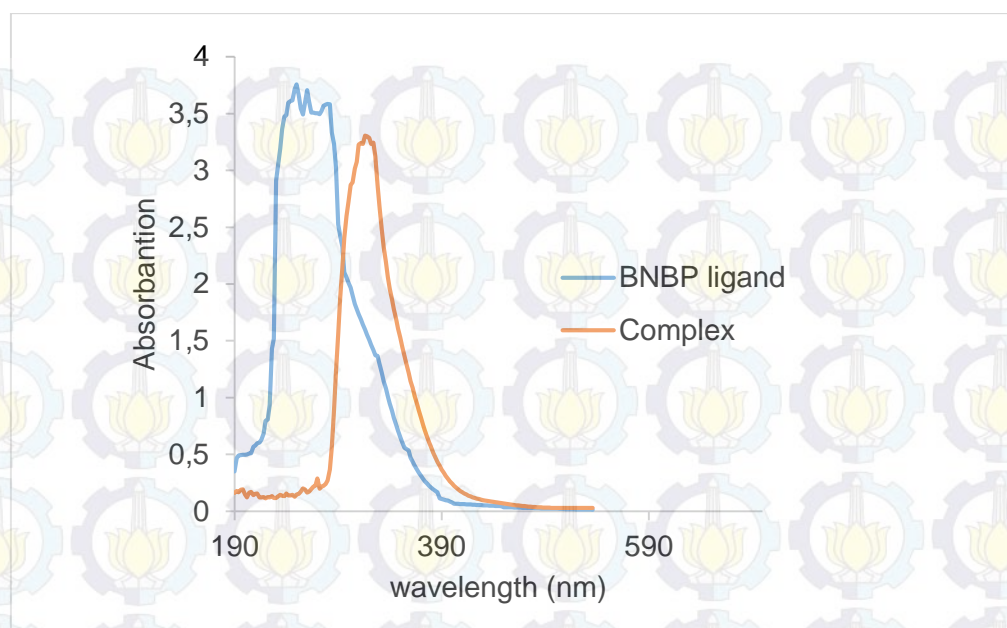


Fig.6 UV-Visible spectra from 2,6-bis(4-nitrobenzamido)pyridine and complex

CONCLUSION

The metal ion Zn(II) complex of 2,6-bis(4-nitrobenzamido)pyridine is successfully formed. Coordination bond most likely to occur through a nitrogen atom in amide group of 2,6-bis(4-nitrobenzamido)pyridine with Zn(II) ion.

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