Synthesis and Characterization of Tetrakis-aqua-bis-isonicotinamide(itmd)nickel(II) Sulfate

S B Rahardjo¹, S Hastuti¹, N Amanati¹, H Syaima²
¹Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Surakarta, 57126, Indonesia
²Chemistry Graduate Program, Graduate School, Universitas Sebelas Maret, Surakarta, 57126, Indonesia

E-mail: sentotbr@yahoo.com

Abstract. The complex of Tetrakis-aqua-bis-(isonicotinamide)nickel(II) sulfate has been synthesized in 1:2 mole ratio of metal to ligands in methanol. The formula of the complex predicted from analysis nickel content in the complex by Atomic Absorption Spectroscopy (AAS) was Ni(itmd)2SO4(H2O)4. The conductivity of the complex in methanol was measured by conductivity meter correspond to 1:1 electrolyte. Thermal analysis of the complex was determined by Differential Thermal Analyzer (DTA) indicating that the complex contains four H2O molecules as ligands. The magnetic susceptibility measurement showed that the complex was paramagnetic with \(\mu_{\text{eff}} = 3.02\) BM. The electronic spectra of the complex appear due to two transition peak on \(\lambda = 398\) nm and 664 nm. The Infrared spectra showed a shift of NH2 stretching vibration of Ni(itmd)2SO4(H2O)4. These facts indicated that these functional groups were coordinated to the center ion of the complexes. The proposed structure of the complex was octahedral therefore the possibility formula of this complex was [Ni(itmd)2(H2O)4]SO4.

1. Introduction

Isonicotinamide (itmd), shown in Figure 1, has function as strong anti-tubercular, fibrinolytic, anti-pyretic, and anti-bacterial [1-3]. That pyridine derivative with an amido group(–CONH2) is often used in the manufacture of drugs due to its strong pharmacological effects [1]. Therefore, it is so easily to obtained. Metal complexes of biologically important ligands sometimes have more effective activity than the free ligands [4-6]. Isonicotinamide can also be used as ligand because it has electrons donor atoms. It is reported that thiocyanate anion and one neutral isonicotinamide ligand forming complex with zinc as central metal ion shown in Figure 2 [7].

![Figure 1](image1.png)  
**Figure 1**. Stucture of isonicotinamide

![Figure 2](image2.png)  
**Figure 2**. Stucture of [Zn(SCN)2(C6H6N2O)2]
Nickel is a metal transition element and abundant the most as Nickel(II) [8]. Ni(II) is considerable to learn due to their stability and abundance in nature [9]. The synthesized nickel(II) complex may form several geometries such as square-planar [10] or tetrahedral [11], square-pyramidal [12], trigonal-bipyramidal [13], and octahedral [14-15]. The most common geometry of nickel(II) complex geometry is octahedral and square-planar [8]. In this work, we learn synthesis and the formation of the nickel complex with isonicotinamide. Thus, the complex is characterized by several instrumental analysis to know the formula, electronic spectra, and magnetic property of the complex. We also determine the probability of the functional group in isonicotinamide that bind to nickel ion.

2. Experimental

2.1. Materials

The chemicals and solvents were of reagent grade and used without further purification. All chemicals such as isonicotinamide, NiSO₄·6H₂O, FeSO₄·7H₂O, CuCl₂·2H₂O, NiCl₂·6H₂O, CuSO₄·6H₂O, AlCl₃·6H₂O, and nitric acid were purchased from E. Merck.

2.2. Physical measurements

Spectra UV-VIS of metal complex and NiSO₄·6H₂O were recorded in methanol solvent using UV-Vis Double Beam Shimadzu PC 1601 spectrophotometer. The nickel content was determined by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. The presence or absence of H₂O molecules in the complex was estimated from the results of thermal analysis using Differential Thermal Analyzer Shimadzu 50. Molar conductivity (Λ*m) of 1 mM complex and standard solution in water were measured on Jenway CE 4071 conductivity meter at 25 °C. The magnetic moment was measured using Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance. Infrared spectra were recorded on Prestige-21 Shimadzu spectrophotometers as KBr pellets in the frequency range of 4000–450 cm⁻¹.

2.3. Synthesis of Ni(II) complex

NiSO₄·6H₂O (0.263 g; 1 mmol) in methanol (5 mL) was added dropwise on isonicotinamide (0.244 g; 2 mmol) in methanol (20 mL) while continuously stirring for ± 2 hours. The solution is allowed to stand for 2 days until a precipitate was formed. The precipitate formed was filtered, washed with cold methanol then dried in a desiccator.

3. Result and Discussion

3.1. Formation of the complex

The electronic spectra of the formed complex in methanol are shown in Figure 3.

![Figure 3. Electronic spectra the complex (a) and NiSO₄·6H₂O (b) in methanol](image-url)
Figure 3 shows the UV-Vis spectra of the complex and NiSO₄·6H₂O in methanol. The absorption spectra of the nickel and the produced compound were shown in two peaks. It is similar with the electronic spectra of the nickel and nickel complex reported by Rahardjo et al. [16]. The maximum wavelength shifted from 735 and 402 nm (NiSO₄·6H₂O) to 664 and 398 nm (Ni-itmd). The shifting of complex wavelength toward smaller than metal ion showed the formation of the complex. It indicated that itmd changes molecules of water and bind to nickel ion.

3.2. Analysis of the amount of nickel with Atomic Absorption Spectroscopy (AAS)
The result of nickel content analyzed by AAS in the Ni(II)-itmd complex was 12.60%. If the result of the measurement was compared to the theoretical analysis shown in Table 1, it could be predicted that the formula of Ni(II)-itmd complex. The different value of theoretical calculation and experiment by AAS was sometimes happen in the research [17-18]. Therefore, the formula of the formed complex was close to Ni(itmd)₂SO₄(H₂O)₆. It needed thermal analysis methods to confirm the number of presence of water molecules as well as the state whether as hydrates or ligands.

| Empirical Formula | Mr | % Nickel |
|-------------------|----|----------|
| Ni(itmd)₂SO₄(H₂O)₂ | 435.04 | 13.50 |
| Ni(itmd)₂SO₄(H₂O)₃ | 453.06 | 12.96 |
| Ni(itmd)₂SO₄(H₂O)₄ | **471.07** | **12.46** |
| Ni(itmd)₂SO₄(H₂O)₅ | 489.09 | 12.00 |
| Ni(itmd)₂SO₄(H₂O)₆ | 507.10 | 11.58 |

3.3. Analysis of electrical conductivity
The results of molar conductivity measurement of the standard solution and complex in water are shown in Table 2. Molar conductivity of the complex was 158 ± 2 S cm² mol⁻¹. If the result was compared to the standard solution, the conductivity of the Ni(II)-itmd complex was close to the electrical conductivity of FeSO₄·7H₂O, CuSO₄·5H₂O, and NiSO₄·6H₂O. The value of the measurement was consistent with the 1:1 electrolyte, indicating that the SO₄²⁻ ions were not coordinated to Ni²⁺.

| Solution | Λₘ (S cm² mol⁻¹) | Cation:anion Charge |
|----------|-----------------|---------------------|
| Water    | 0               | -                   |
| FeSO₄·7H₂O | 103 ± 1        | 1:1                 |
| CuSO₄·5H₂O | 174 ± 2        | 1:1                 |
| NiSO₄·6H₂O | 147 ± 2        | 1:1                 |
| CuCl₂·2H₂O | 216 ± 1        | 2:1                 |
| NiCl₂·6H₂O | 252 ± 1        | 2:1                 |
| AlCl₃·6H₂O | 315 ± 1        | 3:1                 |
| Ni(II)-itmd | **158 ± 2**  | **1:1**             |

3.4. Thermal analysis
The result of Differential Thermal Analysis (DTA) was shown at Figure 4. There was no endothermic peak at about 100 °C, but there was an endothermic peak at 212.42 °C. Lattice water molecules would release at about 100 °C as water boiling point. This peak indicated the release of coordinated H₂O from the Ni(II)-isonicotinamidine complex. Four molecules of water in the complex acted as ligands.
Thus, at 401.08 °C there was an exothermic peak which indicating the occurrence of sulfate ion decomposition [19]. Therefore, the formula of the complex was [Ni(itmd)\(_2\)(H\(_2\)O)\(_4\)]SO\(_4\), namely tetrakis-aqua-bis-(isonicotinamide)nickel(II) sulfate.

![Figure 4. Thermogravimetric/differential thermal analysis spectra](image)

3.5. Infrared analysis
Table 3 shows the infrared analysis of isonicotinamide and Ni(II)-itmd complex. This indicated that the coordinated -NH\(_2\) group of isonicotinamide at the Ni(II) central atom. The smaller wavenumber than isonicotinamide was possible due to the delocalized electrons in the sixth circumference therefore a large enough force was required to push the electron density towards -NH\(_2\). The N-H bond became long and the vibrational energy was small. The shift towards smaller wave numbers of the N-H groups also occurred in the [NiL\(_2\)](ClO\(_4\))\(_2\), L= uramido benzoic acid, from 3224 cm\(^{-1}\) to 3125 cm\(^{-1}\) [20].

| Compounds          | \(\nu\) N-H bending | \(\nu\) C=O cyclic | \(\nu\) C=N aromatic |
|--------------------|---------------------|--------------------|---------------------|
| Isonicotinamide    | 3371                | 1670               | 1597                |
|                    | 3302                |                    | 1555                |
| Ni(II)-itmd        | 3267                | 1682               | 1609                |
|                    |                     |                    | 1555                |
|                    |                     |                    | 976                 |

3.6. Magnetic properties (\(\mu_{\text{eff}}\))
The effective magnetic moment value (\(\mu_{\text{eff}}\)) of the Ni(II)-itmd complex was 3.02 ± 0.09 B.M. The value showed the paramagnetic complex with two unpaired electrons. It was reported that nickel complexes with a value of magnetic moment 3.0, 3.1, 3.2, and 3.3 B.M. forming octahedral geometry [20-21]. The result of the magnetic moment value 2.8-3.5 in the complex of nickel showed octahedral structure [22]. Therefore, the Ni(II)-itmd complex was predicted to form octahedral geometry.

3.7. Electronic spectra
The solution UV–Vis spectrum of the nickel complex showed two peaks at 664 and 398 nm. Basically, the octahedral complex Ni(II) has three electronic transitions \(^3\)A\(_{2g}\)→\(^3\)T\(_{2g}\) (F), \(^3\)A\(_{2g}\)→\(^3\)T\(_{1g}\) (F) and
$^{3}A_2g \rightarrow ^{3}T_{1g}$ (P) in the region 10,000 nm, 600 nm and 400 nm which appear as three peaks in the UV-Vis spectrum [8]. Sometimes the transitions are not visible and just appear two transitions. Tetrakis(2-amino-3-methylpyridine)di(aqua)nickel(II) also showed two transitions at 620 nm (16116 cm$^{-1}$) and 375 nm (26630 cm$^{-1}$). The complex formed octahedral geometry [21]. It was assumed that Ni(II)-itmd complex forming octahedral geometry as well.

3.8. Proposed structure

From all of the characterization analysis above, the proposed structure of the Ni-itmd complex is shown in Figure 5.

![Proposed structure of \( [\text{Ni(itmd)}_2(\text{H}_2\text{O})_4]\text{SO}_4 \).](image)

4. Conclusion

The Ni-itmd complex, namely tetrakis-aqua-bis-(isonicotinamide)nickel(II) sulfate, could be synthesized from NiSO$_4$·6H$_2$O and isonicotinamide in refluxing methanol with a mole ratio of metal to ligand = 1:2. The formula of the complex was \([\text{Ni(itmd)}_2(\text{H}_2\text{O})_4]\text{SO}_4\). The ligands were coordinated to central metal ion through –NH$_2$ group in the isonicotinamide and O-H group of water molecules. The complex was paramagnetic. It had two peaks of UV-Vis absorption at 664 and 398 nm. It was indicated that the complex forming octahedral geometry.

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