Synthesis and characterization of Mono-Aqua-Pentakis (Isonicotinic Acid) Nickel (II) Sulfate Trihydrate

H Syaima¹, S B Rahardjo*² and N Amanati²

¹Chemistry Graduate Program, Graduate School, Universitas Sebelas Maret, Surakarta, 57126, Indonesia
²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sebelas Maret, Surakarta, 57126, Indonesia

*Corresponding email: husna_syaima@yahoo.com, *sentotbr@yahoo.com

Abstract. A complex of nickel (II) with isonicotinic acid (asint) was successfully obtained. The complex was synthesized in 1:2 mole ratio of metal to the ligand in methanol. The percentage of nickel was 6.91% determined by Atomic Absorption Spectroscopy (AAS). Therefore, the predicted formula was Ni(asint)₅SO₄(H₂O)₄. The molar conductivity of the complex was measured by conductivity meter corresponding to 1:1 electrolyte. The thermal analysis of the formed complex was determined by Differential Thermal Analysis (DTA) indicating that the complex contains four water molecules as ligand and hydrates. The magnetic susceptibility measurement showed that the complex was paramagnetic with \( \mu_{\text{eff}} = 3.30 \) B.M. Electronic spectra of the formed complex appeared at two transition peaks on \( \lambda = 394 \) nm and 659 nm. The infrared spectra of the complex showed a shift of tertiary N-group absorption in 1234 and 1338 cm⁻¹ compared to isonicotinic acid at 1149 and 1331 cm⁻¹. In addition, the shift also appeared in the -OH group absorption which was to the lower wavenumber at 3371 cm⁻¹ from 3425 cm⁻¹ (isonicotinic acid). This fact indicated that the functional groups were coordinated to the central metal ion. The possibility formula of the complex was \([\text{Ni(asint)}₅(\text{H₂O})]\text{SO₄·3H₂O}\) with octahedral structure.

1. Introduction

Metal complex is a compound composed of a metal as a central atom and ligand as an electron donor. The study of complex formation becomes an interesting thing to learn because the complex formed may provide many benefits in scientific applications such as clinical, analytical, photocatalytic, and medical biology. One example of a complex compound that is considered is the complexity of nickel metal ions. Nickel has 28 atomic numbers and 3d⁸ electron configuration. Nickel is a class VIIIB transition element and most of its existence is as Ni(II) [1]. Complexes of Ni(II) is synthesized to form multiple geometries with coordination number 4, 5 and 6 include a square-planar [2-3] or tetrahedral [4-5], square-pyramidal [6], trigonal-bipyramidal, [7] and octahedral configurations [8-9]. Tetrahedral and trigonal-bipyramid geometries are very rare. The most common nickel (II) complex geometry is octahedral and square-planar [1]. Ni(II) is interesting to learn due to its cheap price, tends to be stable and abundant in nature.

Isonicotinic acid (asint), shown in Figure 1, a multifunctional chelating and/or bridging ligand, has proved to be very powerful for the construction of multi-dimensional metal–organic coordination...
networks [10]. The complexes with asint as ligands have raised interest in fluorescence probing with numerous potential applications for studies of microsecond diffusion and dynamics of membranes [11]. Asint has -N=, -OH and C=O which are possible to donate electrons to Ni(II). Sahin et al. [12] reported a complex synthesis of nicotinamide with Zn$^{2+}$ ions forming [ZnBr$_2$(C$_6$H$_6$N$_2$O)$_2$] with an octahedral structure as shown in Figure 2. Asint has a structure that is similar to isonicotinamide, therefore, it is possible to form a complex with Ni(II).

![Figure 1. The Structure of Isonicotinic Acid](image1.png)

![Figure 2. Complex Structure [ZnBr$_2$(C$_6$H$_6$N$_2$O)$_2$]](image2.png)

In this study, we synthesized a novel complex of Ni(II) with isonicotinic acid and characterized it with the analytical and spectroscopic methods.

2. Experimental
2.1. Materials
The chemicals and solvents were of reagent grade and used without further purification. All chemicals such as CuSO$_4$·5H$_2$O, isonicotinic acid, NiSO$_4$·6H$_2$O, FeSO$_4$·7H$_2$O, CuCl$_2$·2H$_2$O, NiCl$_2$·6H$_2$O, CuSO$_4$·6H$_2$O, AlCl$_3$·6H$_2$O, and nitric acid were purchased from E. Merck.

2.2. Physical Measurements
Spectra UV-VIS of metal complex and NiSO$_4$·6H$_2$O 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 H$_2$O molecules in the complex was estimated from the results of thermal analysis using Differential Thermal Analyzer Shimadzu 50. Infrared spectra were recorded on Prestige-21 Shimadzu spectrophotometers as KBr pellets in the frequency range of 4000–450 cm$^{-1}$. Molar conductivity (Λ*m) of 1 mM complex and standard solution in water were measured on Jenway CE 4071 conductivity meter at 25 $^\circ$C. The magnetic moment was measured using Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance.

2.3. Synthesis of Ni(II) Complex
NiSO$_4$·6H$_2$O (0.263 g; 1 mmol) was dissolved in methanol (5 mL) then added dropwise on isonicotinic acid (0.269 g; 2.2 mmol) in hot methanol (20 mL). The mixture was refluxed for ± 2 hours. The solution was concentrated to ± 20 mL then allowed to stand for 2 days. The obtained greenish solids were filtered off, washed with methanol and then dried in a desiccator.

3. Result and discussions
3.1. Formation of The Complex
The electronic spectra of the formed complex in methanol are shown in Figure 3.
Figure 3 shows the shift of the maximum wavelength from 735 and 402 nm (NiSO₄·6H₂O) to 659 (15175) and 394 (253807) nm (Ni-asint). It indicated that asint as the ligand change molecules of water and bind to nickel ion. Thus, the shifting of wavelength toward smaller showed the formation of the complex.

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)-asint complex was 6.92%. If the result of the measurement is compared to the theoretical analysis shown in Table 1, it can be predicted the formula of Ni(II)-asint complex. The different value of nickel content based on theoretic and experiment is generally happen in the research [13]. This case happened in the percentage of nickel in the complex of Ni(II) with 6-amino benzothiazole derivative. Theoretically, it was 7.41 % but based on experiment 7.49 % [15]. It needs more methods to confirm the number of presence of water molecules as well as the state whether as hydrates or ligands, such as thermogravimetry and differential thermal analysis. Therefore, the formula of the formed complex is close to Ni(asint)₅SO₄(H₂O)₄.

Table 1. Percentage of Nickel in The Complex Theoretically

| Empirical Formula | Mr      | % Ni     |
|------------------|---------|----------|
| Ni(asint)₅SO₄(H₂O)₃ | 824.37  | 7.12     |
| Ni(asint)₅SO₄(H₂O)₄ | 842.38  | 6.97     |
| Ni(asint)₅SO₄(H₂O)₅ | 860.40  | 6.82     |

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. If both results compared, the conductivity of the Ni(II)-asint complex is close to the electrical conductivity of FeSO₄·7H₂O, CuSO₄·5H₂O, and NiSO₄·6H₂O. The value of the measurement is consistent with the 1:1 electrolyte, indicating that the SO₄²⁻ ions are not coordinated to Ni²⁺.
Table 2. Molar Conductivity of Metal Salts and Ni(II)-asint in Water

| Solution         | \( \Lambda_m \) (S cm\(^2\) mol\(^{-1}\)) | Cation: Anion Charge |
|------------------|---------------------------------|---------------------|
| Water            | 0                               | -                   |
| FeSO\(_4\)·7H\(_2\)O | 103.00 ± 1.00                   | 1:1                 |
| CuSO\(_4\)·5H\(_2\)O | 173.67 ± 1.82                   | 1:1                 |
| NiSO\(_4\)·6H\(_2\)O | 147.33 ± 1.82                   | 1:1                 |
| CuCl\(_2\)·2H\(_2\)O | 216.00 ± 0.47                   | 2:1                 |
| NiCl\(_2\)·6H\(_2\)O | 252.00 ± 0.82                   | 2:1                 |
| AlCl\(_3\)·6H\(_2\)O | 315.00 ± 0.82                   | 3:1                 |
| Ni-asint         | 146.83 ± 4.18                   | 1:1                 |

3.4. Thermal Analysis

Differential Thermal Analysis (DTA) showed the peak of endotherm at temperature 74.37°C (Heat = -0.55 J) and 148.01°C (Heat = -0.69 J), shown in Figure 4. It indicated the evaporation of water molecules as hydrates and the ligand. It is reported that decomposition step at 60-100 °C is assignable to the removal of co-crystallized water molecules [15-16]. Complexes of Ni(II) are known in each of the common geometries: octahedral, tetrahedral and square planar. Therefore, nickel may be coordinated to five molecules of asint and one water forming six coordinated complex. The possible structure is [Ni(asint)\(_5\)(H\(_2\)O)]SO\(_4\)·3H\(_2\)O.

![Figure 4. Thermogravimetric/Differential Thermal Analysis Spectra](image)

3.5. Infrared Analysis

Table 3 shows the infrared analysis of isonicotinic acid and Ni-asint complex. It shows the absorption of C = N groups of cyclic pyridine chains in free ligands (1149 cm\(^{-1}\); 1330 cm\(^{-1}\)) having a shift towards larger wavenumbers (1234 cm\(^{-1}\); 1338 cm\(^{-1}\)) after forming the Ni-isonicotinic acid complex. The same result occurs in the complex of metal with Salicyldene-Cefotaxime. It has a pyridine infrared absorption at 1600 cm\(^{-1}\) then shift to 1640 cm\(^{-1}\) after complexing [17]. From the result, we can confirm
the coordination of C=N to nickel ion. This indicates the N-pyridine group is coordinated to Ni(II) central atom, as in the Zn(II)-nicotinamide complex which originally had a free ligand absorption in the region of 1592 cm\(^{-1}\) and 1573 cm\(^{-1}\) shifted to 1603 cm\(^{-1}\) and 1570 cm\(^{-1}\) [10]. Meanwhile, the infrared absorption of -OH in the complex shifted toward lower wave number compared to the ligand. It indicated that -OH also binds to the nickel ion as the ligand. Thus, the spectra of other functional groups do not experience a shift after the formation of the complex.

Table 3. Infrared Spectra of Functional Groups Isonicotinic Acid and The Complex

| Compounds           | \(\nu\) OH | \(\nu\) NH bending | \(\nu\) COH | \(\nu\) C=O | \(\nu\) C=N aromatic |
|---------------------|------------|---------------------|-------------|------------|----------------------|
| Isonicotinic acid   | 3425       | 1616                | 1411        | 1716       | 1149, 1331           |
| Ni(II)-asint        | 3371       | 1616                | 1411        | 1716       | 1234, 1338           |

3.6. Magnetic Properties (\(\mu_{\text{eff}}\))

The effective magnetic moment value (\(\mu_{\text{eff}}\)) of the Ni(II)-asint complex is 3.30 B.M. The effective magnetic moment value (\(\mu_{\text{eff}}\)) shows the paramagnetic complex with two unpaired electrons. The result of measuring the magnetic moment value in the complex [Ni(L)\(_2\)]\(\cdot\)2H\(_2\)O with L = Schiff Base ligand from 1-amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one with 2-hydroxy-naphthaldehyde in the range 2.8-3.5 B.M. octahedral structure [18]. It is reported by Mukherjee et al. [19] that nickel complexes with a value of magnetic moment 3.0, 3.2, and 3.3 B.M. forming octahedral geometry shown in Table 4. Therefore, the Ni (II)-asint complex is also assumed to be octahedral.

Table 4. Magnetic Moment Value of Nickel Complexes

| Complexes                          | Magnetic Moment Value (B.M.) | Geometry   |
|------------------------------------|-----------------------------|------------|
| [Ni(HSalpn)(NCS)(H2O)]\(\cdot\)H2O | 3.3                         | Octahedral |
| [Ni(HSalpen)(NCS)]                 | 3.0                         | Octahedral |
| [{Ni(Salpen)}\(_2\)Ni(NCS)\(_2\)] | 3.3                         | Octahedral |
| {Ni(Salen)}\(_2\)Ni(NCS)\(_2\)    | 3.2                         | Octahedral |

3.7. Electronic Spectra

The solution UV–Vis spectrum of the formed complex showed two peaks at 659 and 394 nm shown in figure 3. The octahedral complex Ni(II) has three electronic transitions \(^3\)A\(_{2g}\)\(\rightarrow\)\(^3\)T\(_{1g}\) (F), \(^3\)A\(_{2g}\)\(\rightarrow\)\(^3\)T\(_{1g}\) (F) dan \(^3\)A\(_{2g}\)\(\rightarrow\)\(^3\)T\(_{1g}\) (P) which appear as three peaks in the UV-Vis spectrum [1]. The three peaks of the UV-Vis spectra of the octahedral complex Ni(II) are in the vicinity of 10,000 nm, 600nm and 400nm [20]. However, the Ni(II)-isonicotinic acid only shows two transition peaks. The transitions are not visible because they are outside the range of the UV-Vis spectrophotometer used. Tetrakis (2-amino-3-methylpyridine)di(aqua)nickel(II) also showed two transitions at 620 nm (16116 cm\(^{-1}\)) and 375 nm (26630 cm\(^{-1}\)) indicating octahedral geometry [21]. Another octahedral complex of nickel shows two transition peaks of UV-Vis as well [22].

3.8. Proposed Structure

From all of the characterization analysis above, the proposed structure of the complex shown in Figure 5.
4. Conclusion
The Ni(II) complex can be synthesized from NiSO$_4$·6H$_2$O and isonicotinic acid in refluxing methanol with a mole ratio of metal to ligand = 1:2. The complex formula is $[\text{Ni(asint)}(\text{H}_2\text{O})]\text{SO}_4\cdot3\text{H}_2\text{O}$, namely mono-aqua-pentakis (isonicotinic acid) nickel(II) sulfate trihydrate. The ligands are coordinated to central metal ion through N-pyridine in the isonicotinic acid and -OH group of water. The complex is paramagnetic and has two peaks at maximum UV-Vis absorption of 659 and 394 nm. It is indicated that the complex forming octahedral geometry.

5. References
[1] Lee J D 1994 Concise Inorganic Chemistry Fourth Edition (London: Chapman and Hall)
[2] Routaray A, Mantri S, Nath N, Sutar A K and Maharana T 2016 Polyhedron 119 335-41
[3] Takjoo R, Centore R, Akbari A and Ahmadi M 2014 Polyhedron 80 243-49
[4] Routaray A, Mantri S, Nath N, Sutar A K and Maharana T 2015 Spectrochim Acta A Mol Biomol Spectrosc. 139 6-404
[5] Masoud M S, Ali A E, Elasala G S and Kolkaila S A 2017 Journal of Chemical and Pharmaceutical Research 9(4) 171-79
[6] Allali M, Ichou Y, Allali N, Zarrouk A and Habbadi N 2016 J. Mater. Environ. Sci. 7(6) 2042-50
[7] Chastain B B, Rick E A, Pruett R L and Gray H B 1968 J. Am. Chem. Soc. 90(15) 3994–4000
[8] Pahonțu E, Julea F, Chumakov Y, Petrenco P, Roșu T and Gulea A 2015 Journal of Organometallic Chemistry 836–837 44–55
[9] Nikiforov A A, Eremin E A, Gurzhii V V, Misharev A D, Medvedskii N L, Ponyaev A I and Belyaev A N 2017 Russian Journal of Coordination Chemistry 43 269–77
[10] Liu B, Xu L and Guo G 2006 Journal of Solid State Chemistry 179 883–90
[11] Li L, Castellano F N, Gryczynski I and Lakowicz J R 1999 Chem. Phys. Lipids 99 1
[12] Sahin E, Ide S, Atac S and Yurdakul S 2002 Journal of Molecular Structure 616 253-58
[13] Ilies D, Pahontu E, Shova S, Gulea A and Rosu T 2013 Polyhedron 51 307–15
[14] Daravath S D, Kumar M P, Rambabu A, Vamsikrishna N, Ganji N and Shivaraj 2017 Journal of Molecular Structure 1144 147-158
[15] Abdolmaleki S and Ghadermazi M 2017 Inorganica Chimica Acta 461 221–32
[16] Kavitha N and Lakshmi P V A 2015 Journal of Saudi Chemical Society 21 S457-S466
[17] Anacona J R, Johan C and Ovidio A A 2013 International Journal of Inorganic Chemistry http://dx.doi.org/10.1155/2013/108740
[18] Sonmez M 2003 Inorganic Chemistry 77 397-402
[19] Mukherjee P, Biswas C, Drew M G B and Ghosh A 2007 Polyhedron 26 3121–28
[20] Sharpe A G 1992 *Inorganic Chemistry 3rd Edition* (New York: John Willey and Sons Inc.)
[21] Rahardjo S B and Aditya H P 2017 *IOP Conf. Series: Materials Science and Engineering* 17 012048 doi:10.1088/1757-899X/172/1/012048
[22] Vashi R T, Shelat C D and Patel H 2010 *International Journal of Current Pharmaceutical Research* 2(3) 57-60

**Acknowledgement**
The authors gratefully express acknowledgments to Ministry of Research, Technology and Higher Education (RISTEKDIKTI) of the Republic of Indonesia for financial support.