Synthesis and Characterization Complex Nickel(II) with Diphenylamine

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Abstract. Ni(NO₃)₂.6H₂O and diphenylamine formed a complex compound in 1:6 mole ratio of metal to ligand in methanol. The forming of the complex was indicated by shifting of maximum wavelength in UV-Vis spectra. Analysis of the nickel percentage in the complex by Atomic Absorption Spectroscopy (AAS) showed an empirical formula of the complex was Ni(diphenylamine)₄(NO₃)₂.6H₂O. The conductivity measurement of the complex showed the charge ratio of cation and anion = 1:1. It meant that NO₃⁻ was coordinated to the Ni²⁺ center ion and likewise as a counter ion. The formula of complex was approximated [Ni(diphenylamine)₄(NO₃)(H₂O)](NO₃)(5H₂O). Based on infrared spectra, it revealed diphenylamine as monodentate ligand which bind to nickel(II) through the secondary NH functional groups. Electronic spectra showed a transition peak at 25252 cm⁻¹ and 13802 cm⁻¹ which indicating octahedral geometry. The complex was paramagnetic with µₑₑ= 2.99 BM.

1. Introduction
Coordination chemistry is basic chemistry of metal ions which receive electron pairs from ligands around it. Coordination compounds provide a wide range of colors and coordination numbers of metal ions exhibited their structure [1]. Nickel is one of transition metals and abundance in nature as nickel(II) because more stable than nickel(0), nickel(I), nickel(III), and nickel(IV) [2-4]. The geometry formed by the nickel (II) complex varies, including square planar [5,6], tetrahedral [6], trigonal bipyramidal [7], and octahedral [8]. Meanwhile, the most common of the nickel (II) complex geometry are square planar and octahedral. Each nickel(II) complex with certain ligands has different chemical and physical properties, thus making their investigation very interesting and challenging.

Diphenylamine is a derivative of aniline which has an important role in the pharmaceutical field. It has an electron lone pair in the –NH group as a donor site so that it can act as a ligand (Figure 1).

![Diphenylamine structure](image)
Some ligand compounds that have NH groups bond with their metal ions and form complexes as [Ni(CSH)(H₂O)] [6], [Ni(pbh₂)] [9], and Ni(3,3-thiodiproponic acid bis(4-amino-5-ethylamino-2,3-dimethyl-1-phenyl-3-pyrazoline)(NO₃)]NO₃ [10]. At present, we are studying the synthesis, formation and properties as a result of characterization of nickel complexes with diphenylamine.

2. Experimental
2.1. Materials
All of the chemicals used were of analytical grade and used without further purification. They were purchased from E. Merck.

2.2. Physical measurements
The spectra UV-Vis of metal salt and metal complex was recorded in methanol solvent using UV-Vis Double Beam Shimadzu 1601 spectrophotometer. The nickel content was determined by Atomic Absorption Spectroscopy (AAS) Shimadzu AA-6650. Infrared spectra of ligand and complex were recorded as KBr pellets on Prestige-21 Shimadzu spectrophotometers. The magnetic moment was measured by Magnetic Susceptibility Balance (MSB) Auto Sherwood Scientific 10169. Molar conductivity was measured on conductivity meter Jenway CE-4071.

2.3. Synthesis of Ni(II) complex
The nickel(II) complex was prepared by dissolved diphenylamine (2.03 g, 12 mmol) in methanol (10 mL) followed by adding dropwise 10 mL methanolic solution of nickel nitrate hexahydrate (0.58 g, 2 mmol) with continuous stirring for ±3 h. Then, the resulting solution was evaporated until the volume was ± 10 mL. After ±48 h the green precipitated was filtered off, recrystallized, washed with methanol and dried out under vacuum (1.63 g, 84.33%).

3. Result and Discussion
3.1. Formation of the complex
Figure 2 shows the UV-Vis spectra of the nickel(II) complex and NiNO₃.6H₂O in methanol. The maximum wavelengths shifted from 728 nm and 397 nm (Ni(NO₃)₂.6H₂O) toward smaller wavelengths 724 nm and 396 nm in the Ni(II)-diphenylamine complex. This shifting indicated the formation of the complex and also revealed that diphenylamine was a stronger ligand than H₂O [11].

![Figure 2. Electronic spectra (a) Ni(NO₃)₂.6H₂O (b) Ni(II)-diphenylamine complex in methanol](image-url)
3.2. Analysis of the nickel content with Atomic Absorption Spectroscopy

The content of nickel in the Ni(II)-diphenylamine complex measured by AAS presented a value of 5.92 ± 0.05%. Then, the possibility of complex formula can be obtained by comparing the nickel content of this measurement to the nickel content theoretically as shown in the Table 1. Thus, the formula of the nickel(II) complex could be approximated as Ni(diphenylamine)$_4$(NO$_3$)$_3$.6H$_2$O.

| Empirical Formula | Mr  | % Ni |
|-------------------|-----|-----|
| Ni(dpa)$_4$(NO$_3$)$_3$.4H$_2$O | 931.63 | 6.30 |
| Ni(dpa)$_4$(NO$_3$)$_3$.5H$_2$O | 949.63 | 6.18 |
| Ni(dpa)$_4$(NO$_3$)$_3$.6H$_2$O | 967.63 | 6.07 |

3.3. Analysis of electrical conductivity

The measurements results of Ni(II)-diphenylamine complex and standard electrical conductivity in methanol (10$^{-3}$ M) are shown in the Table 2. The Ni(II) complex electrical conductivity was 14.46 ± 0.16 S.cm$^2$.mol$^{-1}$. The cation and anion charge of Ni(II) complex could be known by comparing the electrical conductivity of the standard and Ni(II)-diphenylamine complex solution. So, it showed that the Ni(II)-diphenylamine complex charge ratio of cation and anion was 1:1 [12]. This meant that Ni(II)-diphenylamine complex was electrolyte where only one nitrate ion (NO$_3^-$) was located as counter ion and other nitrate ion coordinated on Ni(II) central ion.

| Solution       | $\Lambda_M$ (S.cm$^2$.mol$^{-1}$) | Cation : Anion Charge |
|----------------|----------------------------------|-----------------------|
| Metanol        | 0                                |                       |
| NiSO$_4$.6H$_2$O | 7.42                            | 1 : 1                 |
| CuSO$_4$.5H$_2$O | 8.60                            | 1 : 1                 |
| CuCl$_2$.6H$_2$O | 47.16                           | 2 : 1                 |
| NiCl$_2$.6H$_2$O | 53.16                           | 2 : 1                 |
| AlCl$_3$.6H$_2$O | 90.96                           | 3 : 1                 |
| Ni(II)-difenilamin | $14.46 \pm 0.16$                | 1 : 1                 |

3.4. Infrared analysis

The infrared spectra of the complex revealed the characteristic bands of ligand functional groups. In comparison the infrared spectra of Ni(II) complex and diphenylamine, there was a shift towards the lower side in the vibration of the -NH group from 3406 and 3383 cm$^{-1}$ (diphenylamine) to 3403 and 3379 cm$^{-1}$ (Ni(II)-diphenylamine complex). This indicated the nitrogen atom (N) of the secondary amine group coordinated on the Ni(II) center ion. In the infrared spectra of complex, the band arised at 1385 cm$^{-1}$ was the $\nu$(NO$_3^-$) vibration which indicated the presence of the nitrate ion as counter ion as in the complex [Ni(3,3’-thiodipropionicacidbis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline)NO$_3$]NO$_3$ [10]. Moreover, in the infrared spectra were also appeared absorption band of the nitrate group at 1260 cm$^{-1}$ which showed that the nitrate ion coordinated on Ni$^{2+}$ center ion [13].

3.5. Magnetic properties

The effective magnetic moment value ($\mu_{eff}$) of the Ni(II)-diphenylamine complex was 2.99 ± 0.05 BM. This value indicated that there were two unpaired electron so that the complex was a paramagnetic complex. The values of $\mu_{eff}$ 2.9 to 3.3 BM in the nickel complex indicated an octahedral complex [14]. Hence, the Ni(II)-diphenylamine complex was suspected to have an octahedral geometry.
3.6. Electronic spectra

The electronic spectra of the complex were recorded in a methanol. The electronic spectra of the Ni(II) complex exhibited two bands of d-d transition at $\lambda_{\text{max}}$ 13.802 and 25.252 cm$^{-1}$. These correspond to the $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(F)(\nu_{2})$ and $^{3}A_{2g}(F) \rightarrow ^{3}T_{1g}(P)(\nu_{2})$ transitions, serially. These transition revealed that the nickel complex possessed an octahedral geometry [7], supported by their magnetic susceptibility values (2.9-3.3 BM). Therefore the probability of a complex formula was $[\text{Ni(diphenylamine)}_4(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)_2.5\text{H}_2\text{O}$. The structure of the complex is suggested as shown in Figure 3, based on all above results.

![Figure 3](image-url)

**Figure 3.** Suggested structure $[\text{Ni(diphenylamine)}_4(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)_2.5\text{H}_2\text{O}$

4. Conclusion

The Ni(II)-diphenylamine complex could be synthesized from stirring Ni(NO$_3$)$_2$.6H$_2$O and diphenylamine in methanol for 3 hour with 1:6 mole ratio of metal to ligand. The complex formula was $[\text{Ni(diphenylamine)}_4(\text{NO}_3)(\text{H}_2\text{O})](\text{NO}_3)_2.5\text{H}_2\text{O}$. The functional group of ligand coordinated on the Ni(II) center ion was probably nitrogen atom from secondary NH group and forming an octahedral geometry. The complex was paramagnetic had two peaks at maximum wavelength of UV-Vis absorption at 724 nm and 396 nm.

Acknowledgement

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

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