Synthesis and Characterization of Cooper Complexes with 2-Aminobenzothiazole

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Abstract. Complexes of copper(II) with aminobenzothiazole are synthesized by mixing CuSO4·5H2O with aminobenzothiazole in 1:4 mole ratio of metal to ligan in methanol and stirres for three hours. The forming of complex was indicated by the shift of maximum wavelength to the shorter wavelength (823 nm to 731 nm) show transition 2B1g → 2A1g. The formula of complexes are predicted from analysis metal in complexes by Atomic Absorption Spectroscopy (AAS) and cooper content is 9.54%. Electrical conductivity measurements resulted in non-electrolite. Thermogravimetric Analysis/Differential Thermal Analyzer (TG/DTA) showed that the complex contained two H2O molecules. The IR spectral data showed a shift in the absorption of the NH2 functional group indicating that the functional group is coordinated to the Cu(II) monodentately. The nature of the magnetic complex was determined by Magnetic Susceptibility Balance (MSB) which results in μeff was 1.83 ± 0.04 BM indicating that the complex was paramagnetic.

1. Introduction

Benzothiazole was a heterocyclic compound, heterocyclic units typically involve five or six member rings with hetero atoms such as O, N and S which are considered to be more polarized than carbon. Some 2-aminobenzothiazole derivatives which have been successfully synthesized with metal salts to form complexes [1]. Transition metals are often used in complex synthesis because they tend to be more stable and colorful compared to other group metals, such as alkali metals and alkaline earth metals, besides that metal ions can function as antibacterial [2]. In addition, one of the metals that can be complexed is cooper, where the cooper complex has also been developed because of its effective biological properties [3]. Copper (II) complexes have received much attention from previous researchers. Copper (II) metal ions exhibit unique thermodynamic capabilities for N-S-O-ligand to form chelate and have a great affinity for coordination due to their smaller size and higher nuclear charge [4-5].

The complex synthesis of aminobenzothiazole derivative ligands has been investigated by several researchers with various metals. In our research, we focus on formation a new metal complexes with a new structure using N and O donor ligands to build a transition metal complex. So, the research objective of this work provides benefits for designing effective complexes compounds from the
synthesis and characterization of copper metal with aminobenzothiazole ligands derived from 2-aminobenzothiazole with cooper metal from CuSO$_4$·5H$_2$O.

2. Experimental

2.1 Material and chemicals
All components used in this study were used without further purification. The component such as metal salt, ligand, and solvent. The metal complex was prepared from 2-aminobenzothiazole as a ligand and metal salts CuSO$_4$·5H$_2$O in 10 mL methanol

2.2 Physical measurements
Electronic spectra was recorded on a UV-Vis Lambda 25 Perkin Elmer spectrophotometer using methanol in the range of 400–800 nm. Measurements of Cooper content was estimated with Shimadzu AA-6650 Atomic Absorption Spectrophotometer (AAS). Infrared spectra was measured on an FT-IR Prestige-21 Shimadzu spectrophotometer using KBr pellets. Thermal analysis was carried out on a TG/DTA Linseis STA PT-1600 at a temperature ranging from 20 to 600 °C with a heating rate of 10 °C/min. Complex and each standard are dissolved in methanol and made at the same concentration (1.10$^{-3}$ M), and then the electrical conductivity of each solution was measured by conductivity using Jenway CE 4071 conductivity meter. Magnetic susceptibility of the complex was measured using Magnetic Susceptibility Balance Auto Sherwood Scientific 10169.

2.3 Synthesis Metal Complexes
Cooper(II) complexes was synthesized from CuSO$_4$·5H$_2$O (0.249 g, 1 mmol) in methanol (5 mL) with the 2-aminobenzothiazole (0.600 g, 4 mmol) in methanol (5 mL) which was added dropwise and stirrer at room temperature for 3 hours. Then the solution was concentrated until the volume of the solution was moiety and the solution becomes more concentrated. The concentrated solution was allowed to stand for 24 hours and dark green solids was observed. The dark green solids was filtered with filter paper and dried by a desiccator vacuum.

3. Result and Discussion

3.1 Electronic spectra
Cu(II) complex with 2-aminobenzothiazole has been successfully synthesized and resulted in a dark green solid weighing 0.371 gram. An indication of the formation of Cu(II) with 2-aminobenzothiazole is characterized by a shift in the absorption of the maximum wavelength towards shorter (823 nm to 731 nm) indicates the formation of a complex between cooper(II) and aminobenzothiazole which shows d-d transitions $^2B_{1g} \rightarrow ^2A_{1g}$ [6]. The shift in wavelength becomes smaller which indicates that the aminobenzothiazole has ligand strength stronger than H$_2$O so that it can replace the position of the previously coordinated H$_2$O molecule in Cu(II) ions [7]. Spectra electronic of metal and complexes show in Figure 1.
3.2 Formula determination of the complexes

Complex empirical formulas were determined by comparing AAS with theoretical formulas. The result of measuring Cu content in the Cu-abt complex was 9.54%. The measurement results are then compared with theoretical cooper content which has been calculated in a variety of possible complex formulas as shown in Table 1 so that the complex formulas formed can be estimated to be Cu(abt)$_3$(SO$_4$)$_x$.nH$_2$O (n = 2, 3, or 4).

| Empirical formula       | %Cu (theoretical calculation) | %Cu (AAS result) |
|-------------------------|-------------------------------|------------------|
| Cu(abt)$_3$(SO$_4$)$_x$.H$_2$O | 10.11                         | 9.54             |
| Cu(abt)$_3$(SO$_4$)$_x$.2H$_2$O | 9.83                          |                  |
| Cu(abt)$_3$(SO$_4$)$_x$.3H$_2$O | 9.56                          |                  |
| Cu(abt)$_3$(SO$_4$)$_x$.4H$_2$O | 9.31                          |                  |

3.3 Analysis of molar conductivity

The results of electrical conductivity measurements of standard and complex compounds in methanol are shown in Table 2. The complex can be determined by the number of ions by comparing the molar
conductivity of a complex solution with the molar conductivity of a standard solution. The molar conductivity value of Cu(II)-abt was zero that indicate the complex was non electrolyte. This is means that SO$_4$ ion is coordinated on the complexes, not as an counter ion. So the estimated complex formula formed is $[\text{Cu(abt)}_3\text{SO}_4].n\text{H}_2\text{O}$ $(n = 2, 3$ or $4)$.

| Compounds                  | Molar conductance $\Lambda^*_{m}$ (S.cm$^2$.mol$^{-1}$) | Cation: Anion ratio | Number of ions |
|----------------------------|--------------------------------------------------------|---------------------|----------------|
| Metanol                    | 0                                                      |                     |                |
| CuSO$_4$.5H$_2$O           | 8                                                      | 1:1                 | 2              |
| FeSO$_4$.7H$_2$O           | 16                                                     | 1:1                 | 2              |
| Cu(NO$_3$)$_2$.5H$_2$O      | 100                                                    | 2:1                 | 3              |
| Co(NO$_3$)$_2$.6H$_2$O      | 130                                                    | 2:1                 | 3              |
| Cr(NO$_3$)$_3$.6H$_2$O      | 160                                                    | 3:1                 | 4              |
| Cu(abt)$_3$(SO$_4$).nH$_2$O | 0                                                      | 0                   | Non-electrolit |

3.4 Thermogravimetric and Differential Thermal Analysis
Thermogravimetry spectra show an reduction compound mass 5.65 % at a temperature under 100 °C indicating the release of H$_2$O molecules in the complex $[\text{Cu(abt)}_3(\text{SO}_4)].n(\text{H}_2\text{O})$ $(n = 2,3,4)$ [8]. From the calculation mass reduction, it was estimated that the compound lost in this temperature range is two H$_2$O molecule. From the thermogravimetry ($TG$) and differential thermal analysis (DTA) can be expected that the empirical formula is $[\text{Cu(abt)}_3(\text{SO}_4)].2(\text{H}_2\text{O})$. 
3.5 Infrared Spectra

The wave number shift of functional groups from 2-aminobenzothiazole free ligand and Cu(II)-abt complexes is shown in Table 3.

| Functional groups | Aminobenzothiazole (abt) | Cu(II)-abt |
|-------------------|--------------------------|-------------|
| NH2 primary       | 3423.96                  | 3291.67     |
|                   | 3355.91                  | 3144.10     |
| C=N               | 1633.42                  | 1633.92     |
| O-H               | -                        | 3589.68     |

From Table 3 shows the shift of N primary from aminobenzothiazole-free ligand wave number to Cu(II)-abt complex towards a smaller direction, from 3423.96 cm\(^{-1}\) and 3355.91 cm\(^{-1}\) (aminobenzothiazole ligand) to 3291.67 cm\(^{-1}\) and 3144.10 cm\(^{-1}\) (complex Cu(II)-aminobenzothiazole). The absorption spectra of the primary functional groups NH2 aminobenzothiazole and Cu(II)-aminobenzothiazole complexes are shown in Figure 3. The shift in wave numbers showed that the NH2 functional groups of aminobenzothiazole is coordinated on the Cu(II) central atom.
3.6 Magnetic Properties

The results of measuring the \( \mu_{\text{eff}} \) of the Cu-aminobenzothiazole complexes was 1.83 BM. This value indicates that there are one unpaired electrons so that the complex was paramagnetic [9] and there is no Cu-Cu bond with the value of \( \mu_{\text{eff}} \) less than 1.73 BM [10]. The square planar complex of Cu(II) represent a magnetic moment value is 1.73 to 2.2 BM [11-12], the value of \( \mu_{\text{eff}} \) cooper complex was present in square planar geometry. Based on the result above, the proposed structure of the complex is shown in figure 4.

![Figure 3. Infrared spectra of CuSO\(_4\).5H\(_2\)O and complex Cu(II)-abt](image)

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\text{Figure 4. Suggested structure of } [\text{Cu(abt)}_3(\text{SO}_4)]\cdot2(\text{H}_2\text{O})
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4. Conclusion

The copper (II) complex with 2-aminobenzothiazole has also been successfully synthesized by reacting CuSO\(_4\).5H\(_2\)O metal salts and 2-aminobenzothiazole ligand in methanol in a ration 1:4 of metal to ligand and stiring for 3 hour at room temperature. Shifting the maximum wavelength from 823 nm to 731 nm indicates that the complex has formed. The measurement of cooper content and TG-DTA from the complexes can be to determined of the complex formulas are [Cu(abt)_3(SO_4)].2H_2O. The
value of electrical conductivity measurement of the complexes was non electrolyte so its mean that the SO$_4$ ion coordinated to the metal ion as anion, not as an ion counter. Infrared spectra shows a shift in wave number indicating that the -NH$_2$ group of aminobenzothiazole was coordinated on the Cu(II) central atom. The measurement of complex magnetic moments yields an effect of 1.83 BM indicating an square planar geometry complex.

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