Synthesis and characterization complex Cobalt(II) with sulfadiazine

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Abstract. Complex of cobalt(II) with sulfadiazine has been synthesized in a ratio 6: 1 metal to ligand in methanol. The formation of a complex was characterized by a shift in the maximum wavelength (λmax) to the smaller wavelength (527 nm to 515 nm) which shows transitions 4T₁g(F) → 4A₂g dan 4T₁g(F) → 4T₁g(P). The percentage of cobalt in the complex measured by Atomic Absorption Spectrometer (AAS) showed the complex formula was Co(Sulfadiazine)₃(NO₃)₂(H₂O)ₙ (n = 2,3,4). The conductivity measurement indicated that the complex is 2 to 1 electrolyte. Thermal analysis with Differential Thermal Analyzer (DTA) indicates the presence of H₂O in the complex. The formula of the complex was estimated as [Co(Sulfadiazine)₃(H₂O)₃]NO₃.H₂O. The complex was paramagnetic with μeff = 4.59 – 4.97 BM in high spin state. Infrared spectra show a shift in the absorption of primary NH₂ functional groups indicating that the functional group was coordinated to the central Co²⁺ atom monodentically. The geometry of the complex was probably octahedral.

1. Introduction

Inorganic chemistry research in the medical field has been widely developed through the synthesis of new compounds that are thought to have antibacterial activity [1]. Complex compounds consist of metal ions metals that have d orbitals that have not been fully filled by electrons with ligands that have donor atoms. Many new complex compounds that are successfully synthesized provide better results than their free ligands [2]. Complexes with cobalt metal have better antibacterial activity compared to complexes with copper and nickel metals [3]. Some cobalt complexes are also known to have higher antibacterial activity compared to other transition metals [4].

Sulfadiazine is a derivative of sulfonamides and polydentate ligand, so they can coordinate to metal ions [5]. The electron donor of sulfadiazine is O, N primary, N secondary, and N tertiary in the cyclic chain. The cobalt complex generally has octahedral and tetrahedral geometries, such as in the [Co(H₂O)₆(sul)]₂⁺ (sul = sulindac) complex coordinating from two atoms from O from the ligand and four O atoms from H₂O molecules at Co²⁺ central ion forming geometry octahedral [6]. The Co complex can also have tetrahedral geometry as in the Co(II) with (2-bromo-4-chloro-6(cyclopropyliminomethyl)-phenol) where two atoms O and two atoms N from ligand coordinates on Co²⁺ central ion [7]. Generally, Co (II) has a number of coordination of the complex with octahedral structures. Cobalt complexes may be formed with a variety of ligands, including sulfadiazine.

2. Experimental

2.1. Materials Chemicals

All chemicals used were purchased from E. Merck.
2.2. Physical measurements
Spectra UV-VIS was accomplished on Shimadzu UV-3601 spectrophotometer. The cobalt content was counted by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. Infrared spectra were recorded with Prestige-21 Shimadzu spectrophotometers using KBr. Thermogravimetry (TG) and differential thermal analysis (DTA) Diamond Perkin Elmer analyzer used for analysis thermogravimetric and stability of the metal complex. Electrical molar conductivity (\(\Lambda_m\)) of 1 mM solution in DMF was account on Jenway CE 4071 conductivity meter at 25 °C. The magnetic moment was measured with Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance.

2.3. Synthesis of Co(II) complex
Methanolic solution (10 mL) of Co(NO\(_3\))\(_2\).6H\(_2\)O (3.492 g; 6 mmol) was added dropwise to methanolic solution (20 mL) of sulfadiazine (0.501 g; 1 mmol) with reflux for 24 hours. Co(NO\(_3\))\(_2\).6H\(_2\)O solution initially purple and then after the addition of ligand sulfadiazine, the solution became brown. The solution was then concentrated 1/3 of the previous volume. The precipitate was filtered, then dried in a desiccator for 48 hours.

3. Result and Discussion
3.1. Electronic spectra
The formation of a complex is characterized by a shift in the maximum wavelength in electronic spectra. Spectra Co(NO\(_3\))\(_2\).6H\(_2\)O and Co(II)-Sulfadiazine are shown in Figure 1. The maximum wavelength shift towards the wavelength smaller than 527.5 nm (Co(NO\(_3\))\(_2\).6H\(_2\)O) becomes 515.4 nm (Co(II) -sulfadiazine), indicates the formation of a complex between cobalt(II) and sulfadiazine which shows transitions \(\ ^4\text{T}_{1g}(F) \rightarrow \ ^4\text{A}_{2g}\) dan \(\ ^4\text{T}_{1g}(F) \rightarrow \ ^4\text{T}_{1g}(P)\). Shifting the wavelength uptake in a smaller direction indicates that the sulfadiazine ligand is stronger than H\(_2\)O so that it can replace the coordinated position of H\(_2\)O molecules in Co(II) ions[5].

Figure 1. Electronic spectra of Co(NO\(_3\))\(_2\).6H\(_2\)O (a) and Co(II)-sulfadiazine complex (b)
3.2. Analysis of the cobalt content with Atomic Absorption Spectroscopy (AAS)
Cobalt content in the complex counted with AAS bring out the value of 5.98 ± 0.19%. If the amount results are compared with theoretical cobalt content on various possible complex formulas as shown in Table 1, then the complex formula formed is estimated to be \( \text{Co(Sulfadiazine)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_n \) \((n = 2, 3, \text{or } 4)\). The difference in experimental results with the results of theoretical calculations of Co levels also occurs in the Co complex \((\text{N,N’-bis(2-hydroxybenzylidene)-1,1diaminobutane}) [6]\) which has a difference of 0.02%.

| Table 1. Amount of cobalt in the complex theoretically (%) |
|----------------------------------------------------------|
| Formula                        | Molecular weight (g/mol) | % Cu   |
|--------------------------------|--------------------------|--------|
| \( \text{Co(Sulfadiazine)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_2 \) | 969.75                  | 6.07%  |
| \( \text{Co(Sulfadiazine)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_3 \) | 987.75                  | 5.96%  |
| \( \text{Co(Sulfadiazine)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_4 \) | 1005.75                 | 5.85%  |

3.3. Thermal analysis by TG/DTA
In Figure 2 (green curve) there is an endothermic peak at a temperature of 60.5 °C indicating the release of \( \text{H}_2\text{O} \) molecules in the complex \( \text{Co(Sfdz)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_n \) \((n = 2, 3, 4)\) [7]. This is supported by data from the TGA (Thermogravimetric Analyzer) (blue curve) where there is a reduction in compound mass from 95.6% (temperature 62.6 °C) to 84.3% (temperature 177.8 °C). From the calculation mass reduction, it is estimated that the compound lost in this temperature range (from 62.6 °C to 177.8 °C) is four \( \text{H}_2\text{O} \) molecule. From the thermogravimetry (TG) and differential thermal analysis (DTA) can be expected that the empirical formula is \( \text{Co(Sulfadiazine)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_4 \).

\(0.5 \text{ sec}\)

**Figure 2.** TG/DTA analysis of the complex

3.4. Analysis of molar conductivity
The results of measurements of the molar conductivity of solutions of standard compounds and complex solutions in methanol are represent in Table 2. The electrical conductivity of standard
solutions were de
cide in DMF (10^{-3} M) at room temperature. The number of ions in the complex can be known by comparing the value of the molar conductive power of the complex solution with the standard molar conductivity. The value of electrical molar conductivity of the standard in Table 2 shows that the more ions in the solution the greater the value of the conductivity of the molar. The value of the molar conductivity of Co(II)-sulfadiazine complex approached the value of electrical conductivity of the solution of Co(NO_3)_2.6H_2O and Mn(SO_4)_2.6H_2O with a ratio cation : anion = 1: 1. This indicate that the ion NO\(^-\) acts as an anion because not coor
dinated to the central metal Co(II) [8-9]. Thus, the formula of the complex can be confirmed as [Co(Sfdz)_3(H_2O)_3](NO_3)_2.H_2O.

| Table 2. Molar conductivity of standard and Co(II)-sulfadiazine in DMF |
|-----------------------------|----------------|
| Solution                   | \( \Lambda_m \) (S cm\(^2\) mol\(^{-1}\)) | Total ions |
| DMF                        | 1.15            | -            |
| NaNO\(_3\)                 | 83.15           | 1:1          |
| KNO\(_3\)                  | 89.45           | 1:1          |
| Co(NO\(_3\))\(_2\).6H\(_2\)\(_O\) | 128.50         | 2:1          |
| Mn(SO\(_4\))\(_2\).6H\(_2\)\(_O\) | 156.05         | 2:1          |
| AlCl\(_3\).6H\(_2\)\(_O\)   | 188.95          | 3:1          |
| Al(NO\(_3\))\(_2\).6H\(_2\)\(_O\) | 222.25         | 3:1          |
| Co(Sfdz)_3(NO\(_3\))\(_2\).(H\(_2\)O)_4 | 149.15        | 2:1          |

3.5. Infrared (IR) analysis
The wave number shift of sulfadiazine-free ligand functional groups and Co(II)-sulfadiazine complexes is shown in Table 3.

| Table 3. Infrared absorption band of sulfadiazine and Co(II)-sulfadiazine |
|-------------------------------|----------------|
| Functional groups             | Wave number (cm\(^{-1}\)) |
| Sulfadiazine                  | Co(II)-sulfadiazine |
| -NH\(_2\) primary             | 3423.96          | 3423.15 |
|                                | 3355.91          | 3354.96 |
| -SO\(_2\) asymmetric          | 1325.72          | 1326.32 |
| -SO\(_2\) simetryc            | 1156.63          | 1157.54 |
| C=N                           | 1651.97          | 1652.28 |
| C=C                           | 1492.88          | 1495.73 |

From Table 3 shows the shift of N primary from sulfadiazine-free ligand wave number to Co(II)-sulfadiazine complex towards a smaller direction, from 3355.91 cm\(^{-1}\) (sulfadiazine ligand) to 3354.96 cm\(^{-1}\) (complex Co(II)-sulfadiazine). The absorption spectra of the primary functional groups NH\(_2\) sulfadiazine and Co(II)-sulfadiazine complexes are shown in Figure 3. The shift in wave numbers showed that the -NH\(_2\) functional groups of sulfadiazine is coordinated on the Co(II) central atom.

3.6. Magnetic properties (\(\mu_{\text{eff}}\))
The results of measuring the \(\mu_{\text{eff}}\) of the Co-sulfadiazine complex were 4.61 BM. This value indicates that there are three unpaired electrons so that the complex is paramagnetic [10]. The octahedral complex of Co(II) represent a magnetic moment value is 4.3 to 5.2 BM [11-12], the value of \(\mu_{\text{eff}}\) cobalt complex was present in octahedral geometry. Thus the complex structure [Co(Sfdz)_3(H_2O)_3](NO_3)_2.H_2O is estimated as shown in Figure 3.
Figure 3. Suggested structure of \([\text{Co(Sfdz)}_3(\text{H}_2\text{O})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O})\)

4. Conclusion

Complex \([\text{Co(Sfdz)}_3(\text{H}_2\text{O})_3](\text{NO}_3)_2 \cdot \text{H}_2\text{O}\) can be synthesized by addition sulfadiazine in methanol and Co(II) in methanol in a ratio 6: 1 of metal to ligand and stirring at 60°C during 24 hours. The results of the measurement of Co content in the Co(II)-sulfadizine complex and TG-DTA analysis obtained the complex formula \(\text{Co(Sfdz)}_3(\text{NO}_3)_2(\text{H}_2\text{O})_4\). The measurement of complex electrical conductivity results in a ratio of 2: 1 cation and anion. This means that \(\text{NO}^-\) is not coordinated on \(\text{Co}^{2+}\) and is located as an anion in the complex, so that the complex formula formed \([\text{Co(Sfdz)}_3(\text{H}_2\text{O})_3][\text{NO}_3]_2 \cdot \text{H}_2\text{O}\). Infrared spectra shows a shift in wave number indicating that the -NH₂ group of sulfadiazine is coordinated on the Co(II) central atom. The measurement of complex magnetic moments yields an effect of 4.61 BM indicating an octahedral geometric complex.

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