Facile and rapid synthesis of tetrakis-2-amino-5-methylpyridinecopper(II) chloride pentahydrate

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Abstract. Pyridine and its derivatives are important compounds with tremendous applications. Pyridine derivatives, such as aminopyridine, have been widely investigated concerning their biological activity. It is reported that generally biological activities of the compound increased after complexation. Tetrakis-2-amino-5-methylpyridinecopper(II) chloride pentahydrate has been synthesized facilely in less than five minutes. It was formed by mixing CuCl₂·2H₂O and 2-amino-5-methylpyridine in 1:4 mole ratio in ethanol at room temperature. The complex was characterized to determine its proposed empirical formula and the structure. The forming of the complex was indicated by shifting of maximum wavelength (λmax) of UV-Vis spectra towards smaller than CuCl₂·2H₂O from 850 nm to 675 nm. Atomic Absorption Spectroscopy (AAS) measurement showed the content of copper to be 9.63 % corresponding to the theoretical value of copper content in Cu(2-amino-5-methylpyridine)₄Cl₂·4H₂O (x= 4, 5, or 6). Thermogravimetric Analysis and Differential Scanning Calorimetry (TGA-DSC) showed a mass reduction of 13.02 % which was equivalent to the evaporation of five molecules of lattice water. The cation and anion charge ratio of the complex was 2:1. This four coordinated-complex was paramagnetic with an effective magnetic moment of 1.83 BM. The proposed empirical formula of the complex was [Cu(2-amino-5-methylpyridine)₄]Cl₂·5H₂O.

1. Introduction
Pyridine and its derivatives are interesting compounds among scientists. They are important with tremendous applications in the various fields [1-3]. Pyridine derivatives containing amino groups have been widely investigated concerning their biological activity. It is reported that the compounds posing exciting activity as antibacterial, antiviral, antifungal, and anti-inflammatory agents [4-7]. Further, it is reported that generally biological activities of the compound increased after complexation. Nitrogen atoms and its lone pair electrons in an aromatic environment make the pyridine group and its derivatives interesting compounds for coordination chemistry. Pyridine derivatives can act as a ligand and have been utilized in producing metal complexes with transition metal ions.

In several previous studies, pyridine derivatives containing amino groups were coordinating to different metal centers and different complexes were synthesized. Erdemir et al. (2019) have successfully synthesized Pd(II) complex with 2-aminopyridine through N-pyridine atom [8]. Kartal et al. (2018) prepared Zn(II) and Cd(II) complexes with 3-aminopyridine [9]. Ahmadi et al. (2011) have
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synthesized four novel cobalt complexes with 2-amino-4-methylpyridine, 2-amino-3-methylpyridine, and 2-amino-5-chloropyridine [10].

Copper(II) is stable and often used in many research [11]. Copper is also an important element for all living organisms such as humans, animals, microorganisms, and plants [12-13]. In this study, copper(II) complex with 2-amino-5-methylpyridine was synthesized to determine the empirical complex formula and properties formed.

2. Experimental
2.1. Materials
The chemicals and solvents were reagent grade and used without purification. The chemicals such as 2-amino-5-methylpyridine, nitric acid, CuCl₂·2H₂O, FeSO₄·7H₂O, NiCl₂·2H₂O, CuSO₄·6H₂O, and AgNO₃ were purchased from E. Merck.

2.2. Synthesis of the metal complex
The solution of CuCl₂·2H₂O (0.341 g; 2 mmol) in 10 mL ethanol was added dropwise into a 2-amino-5-methylpyridine solution (0.865 g; 8 mmol) in 15 mL ethanol with constant stirring. The brown solid precipitated. The solid was filtered and then washed with chloroform and ethanol. Then, the solid was dried in a vacuum desiccator over silica gel.

2.3. Instrumentation
The copper content in the complex was determined by Shimadzu AA-665 Atomic Absorption Spectrophotometer. Electronic absorption spectra were obtained with UV-Vis Double Beam Shimadzu PC 1601 spectrophotometer. The thermal behavior of the complex was recorded on Shimadzu 50 Differential Thermal Analyzer within temperature range 30-700 °C. Conductivity was measured on Jenway CE 4071 conductivity meter. The corrected molar magnetic susceptibilities have been measured at room temperature using Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance. Infrared spectra for KBr discs were recorded on Prestige-21 Shimadzu spectrophotometers in the frequency range 4000-450 cm⁻¹.

3. Results and Discussion
3.1. Synthesis of the complex
Complex synthesis is carried out by mixing metals and ligands in a ratio of 1:4 in ethanol. When the metal solution was added dropwise into ligand solution, precipitate immediately formed followed by changing in color, from clear colored reactants into dark brown solid. The obtained yield was 68%. Directly formed deposits are possible due to fast complexing. According to spectrochemical series, C=N and NH₂ group in 2-amino-5-methylpyridine ligand pose high ligand field strength [14]. The complex formed has difference solubility with reactants in ethanol. Therefore, it immediately precipitated. The formation of the complex can be shown in electronic spectra. The maximum wavelength of Cu(II) solution shifted from 850 nm (CuCl₂·2H₂O) to 675 nm (the complex) as shown in figure 1. The presence of blueshift in the spectra was due to the replacement of H₂O molecules in Cu(II) with 2-amino-5-methylpyridine ligands which have greater energy. These UV-Vis spectra are an early indication of complex formation. Then the complex needs further analyzed to determine the formula and characteristics of the complex.
3.2. AAS result
AAS was used to estimate the possible empirical formula of the complex. The theoretical copper content in the complex is compared to the AAS results as shown in Table 1. From the data, the possible formula of Cu(II)-2-amino-5-methylpyridine is Cu(2-amino-5-methylpyridine)nCl2(H2O)m (n = 4, 5 or 6).

Table 1. The copper content in some possible formulas of Cu(II)-2-amino-5-methylpyridine

| The formula of the complex | Theoretic calculation (%) | AAS result (%) |
|----------------------------|----------------------------|---------------|
| 1. Cu(2-amino-5-methylpyridine)nCl2(H2O)4 | 9.94 | 9.67 |
| 2. Cu(2-amino-5-methylpyridine)nCl2(H2O)5 | 9.67 | 9.63 |
| 3. Cu(2-amino-5-methylpyridine)nCl2(H2O)6 | 9.41 | 9.63 |

3.3. Thermal analysis
The thermal behavior of the metal complex was characterized by TGA-DSC technique. The TG thermograms of the complex are represented in Figure 2. The TGA curve of the complex shows one-step decomposition (mass loss: 13.02%) at 32-75°C. It corresponds to the evaporation of five hydrates or lattice water in the complex. It also strengthens by an endothermic process at 66 °C from DSC data. This process also happened in [Cu(Gapentine)(γ-aminobutyric acid)(H2O)3]Cl·H2O at 27-87 °C which corresponding to the dehydration process [15]. The next step of decomposition appeared in the thermogram at the range 133-342 °C. It is probably assigned to the dissociation of the ligand. The third decomposition occurred within the range 352-700 °C appeared as a flat peak due to the last decomposition of the organic compound (ligand) leaving the CuO as a final residue [16].
3.4. Qualitative chloride ion analysis

This analysis was used to determine whether the chloride ions were coordinated to the copper ion or acted counter ions. The testing was performed qualitatively by adding AgNO₃ solution into a complex solution. White solid of AgCl would precipitate according to the reaction [17]:

$$\text{Cl}^- (aq) + \text{AgNO}_3 (aq) \rightarrow \text{AgCl} (s) + \text{NO}_3^- (aq)$$

The results showed a white precipitate when the AgNO₃ solution was added dropwise to a solution of Cu(II)-2-amino-5-methylpyridine. It explained that chloride acted as counter ions.

3.5. Electrical conductivity

Molar conductivity is used to determine the mole ratio of cation and anion and conductivity of the complex. This mole ratio was determined by comparing molar conductivity of the Cu(II) complex to molar conductivity of some known salts in methanol ± 1.10⁻³ M. From data in table 2, molar conductivity of the complex is in the range of 1:2 mole ratio of cation/anion. It means that chloride ions are not coordinated to Cu(II) and acting as counter ions. Therefore, the proposed formula of the complex is [Cu(2-amino-5-methylpyridine)₂][Cl₂·5H₂O].

| Solution                  | Λ_m (S.cm².mol⁻¹) | Mole ratio of cation/anion |
|---------------------------|-------------------|---------------------------|
| CuSO₄·5H₂O                | 2 ± 0.1           | 1 : 1                     |
| FeSO₄·7H₂O                | 12 ± 0.1          | 1 : 1                     |
| NiCl₂·6H₂O                | 170 ± 2.0         | 1 : 2                     |
| CuCl₂·2H₂O                | 92 ± 1.5          | 1 : 2                     |
| Cu(II)-2-amino-5-methylpyridine | 94 ± 0.2       | 1 : 2                     |
3.6. IR spectra

FTIR spectra of the complex were compared with the free 2-amino-5-methylpyridine as shown in figure 3. The bands attributed to ν(N-H) vibration appear around 3444 and 3335 cm⁻¹ for the ligand. These bands appear at the complex but shift into the absorption of 3444 and 3338 cm⁻¹.

![FTIR spectra of 2-amino-5-methylpyridine and the complex](image)

Figure 3. FTIR spectra of 2-amino-5-methylpyridine and the complex

It was also found that the bands due to the C=N group appeared at 1630 cm⁻¹ in 2-amino-5-methylpyridine and 1660 cm⁻¹ in the complex. It suggests that C=N suggesting its involvement in the coordination sphere. Shifting of coordinating group into higher wavenumbers also happen at other complexes [19-20]. The absorption of ν(N-H) of the ligand is almost not shifted. It shows that N-H group does not participate in chelation. Based on IR data, it was concluded that 2-amino-5-methylpyridine acting as the monodentate ligand.

3.7. Magnetic properties ($\mu_{\text{eff}}$) and electronic spectra

The magnetic and electronic measurements can be used to estimate the geometry of the complex [16]. The value of the magnetic moment (1.83 B.M) of this complex confirmed the square planar geometry. Complex of Cu(II) with 7-((1H-benzo[d]imidazol-2-yl)diazenyl)-5-nitroquinolin-8-ol. has magnetic moment value 1.84 B.M which assigned to square planar geometry [16, 21-22]. The spectrum of Cu(II) complex displayed an absorption band at 675 nm assigned to d-d copper transition (sum of electronic copper transitions: $^2B_{1g} \rightarrow^2B_{2g}$, $^2B_{1g} \rightarrow^2E_g$, and $^2B_{1g} \rightarrow^2A_{1g}$ transition). This also assumes that the complex forming square planar geometry. It is reported that square planar copper complexes have a maximum wavelength of around 600 nm [21-24]. From the data, the proposed structure of [Cu(2-amino-5-methylpyridine)$_4$]Cl$_2$·5H$_2$O is shown in figure 4. This $\mu_{\text{eff}}$ value is similar for paramagnetic Cu(II) complexes supporting the exclusion Cu-Cu [25].
4. Conclusion
The synthesis and the spectroscopic characterization of copper complex constructed by 2-amino-5-methylpyridine ligands have been described. The complex is estimated to be mononuclear square planar complex with empirical formula $[\text{Cu(2-amino-5-methylpyridine)}_2]\text{Cl}_2\cdot5\text{H}_2\text{O}$. The paramagnetic complex was obtained after coordination of N-pyridine from the ligand with the copper ion.

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