Synthesis and Characterization of Tetrakis(2-amino-3-methylpyridine)copper(II) Sulfate Tetrahydrate

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Abstract. The complex of Tetrakis(2-amino-3-methylpyridine)copper(II) sulfate tetrahydrate has been synthesized in a ratio of 1:6 metal to ligand in methanol. The percentage of copper in the complex measured by Atomic Absorption Spectrometer (AAS) showed the complex formula was Cu(2-amino-3-methylpyridine)₄SO₄(H₂O)ₙ (n = 3, 4, or 5). The analysis of TG/DTA showed that 1 mole of complex contains 4 moles of H₂O. The conductivity measurement indicated that the complex is in 1 to 1 electrolyte. The formula of the complex was estimated as [Cu(2-amino-3-methylpyridine)₄]SO₄·4H₂O. The complex was paramagnetic with µeff of 1.85 BM. The UV-Vis spectra showed a band peak at 730 nm with an electronic transition Eg→T₂g. IR spectral data indicated that the functional groups of N-pyridine 2-amino-3-methylpyridine coordinated to ion Cu(II). The geometry of the complex was probably square planar.

1. Introduction
Pyridine derivative which has antibacterial activity [1] is able to act as ligands. It is due to the availability of free electron pair to bond with a metal ion. Pyridine derivative ligands can form complexes with different types of donor atoms coordinated to the metal ion. In case the complex of [Ag(2-amino-3-methylpyridine)₂]NO₃, the ligand has an electron donor atom N in the primary amine and N-pyridine. Coordinated donor atoms are N in pyridine [2]. After complexing, the effectivity of ligands as antibacterial increase significantly. The complex of Cu(II)-2,4-dinitro-6(pyridine-2-ylmethylamino)methyl-phenolate has better bactericidal activity than complex of Fe(II), Zn(II), Ni(II) and 2,4-dinitro-6(pyridine-2-ylmethylamino)-methylphenolate as ligands [3]. Therefore, complexing copper ion with pyridine derivative ligands seems promising due to the improvement of both antibacterial activities.

Copper is one of transition metal elements with 3d⁹ electron configuration that can form complexes because they have d orbitals are not fully charged electrons. Copper has the oxidation number of +1 and +2, copper in the form of Cu(II) is more stable than Cu(I). Cu(II) can form a wide variety of geometries in the complex include square planar [4], square pyramidal [5], and octahedral [6] but generally Cu(II) has a coordination number of four bonded to ligands forming complexes with square planar structure.
2. Experimental

2.1. Materials
All chemicals were purchased from E.Merck.

2.2. Physical measurements
The copper content was determined by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. Infrared spectra were recorded on Prestige-21 Shimadzu spectrophotometers using KBr disc. The thermogravimetric analysis of the metal complex was recorded on Thermogravimetric/Differential Thermal Analysis (TG/DTA) Diamond Perkin Elmer analyzer. Spectra UV-VIS was performed on Shimadzu UV-3601 spectrophotometer. Molar conductivity ($\Lambda^m$) of 1 mM solution in methanol was measured 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 Cu(II) complex
Methanolic solution (10 mL) of CuSO$_4$·5H$_2$O (0.748 g; 3 mmol) was added dropwise to methanolic solution (20 mL) of 2-amino-3-methylpyridine (1.944 g; 18 mmol) with constant stirring for 3 hours. CuSO$_4$·5H$_2$O solution initially blue and then after the addition of ligand 2-amino-3-methylpyridine, the solution became green. The solution was then concentrated 1/3 of the previous volume. Furthermore, the solution was diffused using diethyl ether and left to stand for 72 hours. The precipitate was filtered, then dried in a desiccator for 48 hours.

3. Result and Discussion

3.1. Electronic spectra
Figure 1 shows the shift of CuSO$_4$·5H$_2$O maximum absorption wavelength (818 nm) towards smaller wavelengths in the complex Cu(II)-2-amino-3-methylpyridine (730 nm). Shifting $\lambda_{max}$ indicates the formation of the complex due to the substitutions of H$_2$O molecules with 2-amino-3-methylpyridine. It was estimated that 2-amino-3-methylpyridine have greater powers than the H$_2$O. Electronic spectra of the complex [Cu(2-amino-3-methylpyridine)$_4$]SO$_4$·4H$_2$O shows a wide absorption at $\lambda_{max}$ 730 nm (13700 cm$^{-1}$). A low-intensity absorption band of a copper complex at 740 nm is assigned to the Eg→T$_{2g}$ transition which attributed to square planar geometry [7], so is 720 nm [8]. Therefore, it indicated the square planar geometry around metal ion in the formed complex.

![Figure 1. Electronic spectra of CuSO$_4$·5H$_2$O solution (a) and the complex solution (b)](image_url)

3.2. Analysis of the amount of copper with Atomic Absorption Spectroscopy (AAS)
AAS was used to determine the total copper content of the complex shown in table 1. The result of copper content in the complex was 9.53±0.06%. This result of the measurements was compared to the
calculation results of the proposed complex formula. It can be estimated that the complex formula is 
\[ \text{Cu}(2\text{-amino-3-methylpyridine})_4\text{SO}_4(\text{H}_2\text{O})_n \]  (n=3, 4 or 5).

**Table 1.** Percentage of copper in the complex theoretically.

| Empirical Formula                                      | Molecular weight (g/mol) | % Cu |
|--------------------------------------------------------|--------------------------|------|
| Cu(2-amino-3-methylpyridine)_4SO_4(H_2O)_3           | 645.5                    | 9.84 |
| Cu(2-amino-3-methylpyridine)_4SO_4(H_2O)_4           | 663.5                    | 9.57 |
| Cu(2-amino-3-methylpyridine)_4SO_4(H_2O)_5           | 681.5                    | 9.32 |

### 3.3. Thermal analysis by TG/DTA

Thermogram of complex in figure 2 shows the endothermic reaction in the area of 129 °C followed by 10.89% mass reduction in the temperature range 135-174 °C, which corresponds to the loss of four molecules H_2O. Something similar happened at the complex Cu(II)-sepamet that showed a mass reduction in 79.9 to 146.4 °C 9.50 % indicating loss of four molecules of lattice water [9]. The complex [Cu(en)(phen)_2]Br_2·2phen·8H_2O, en=ethylenediamine, phen=[bis (1,10 Phenanthroline) also experienced a reduction in mass at 170 °C indicating the release of H_2O molecules as hydrates [10]. Based on the analysis TG/DTA can be estimated that the complex formula is Cu(2-amino-3-methylpyridine)_4SO_4·4H_2O.

![Figure 2. TG/DTA analysis of the complex](image)

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

### 3.4. Analysis of electrical conductivity

The molar conductivity of the complex and standard solution were determined in methanol (10^{-3} M) at room temperature. The value of molar conductivity is shown in table 2. The molar conductance values of the complex lie in 12.7 ± 0.1 S.cm^2.mol^{-1}, thus indicating that is an electrolyte. By comparing the conductivity values of the complex sample with a molar conductivity of the standard solution, it can be seen that the charge ratio of cationic: anions= 1:1. This shows that the ion SO_4^{2-} is not coordinated to the central metal ion Cu(II) and only acts as an anion [11-12]. Thus, the formula is probably [Cu(2-amino-3-methylpyridine)_4]SO_4·4H_2O.
3.5. Infrared (IR) analysis
In order to find binding modes of the ligand with transition metal ions, infrared spectra of compounds were recorded. Table 3 shows the infrared absorption of functional groups in the ligand and the complex. On comparison of infrared spectra of 2-amino-3-methylpyridine and the complex, the C=N band at 1583 cm\(^{-1}\) in ligand was shifted by 66 cm\(^{-1}\) to a higher frequency on complexation indicated coordination of N-pyridine in 2-amino-3-methylpyridine to the metal ion. It was evidenced by an absorption at 475 cm\(^{-1}\) which indicated the presence of Cu-N bond. A similar case also occurred in the complex \([\text{Cu}(\text{2-amino-3-methyl-pyridine})_4 \text{SO}_4 \cdot 4\text{H}_2\text{O}]\) which has an absorption of N-pyridine at 1600 cm\(^{-1}\) and shift towards higher at 1640 cm\(^{-1}\) in the complex and there was a new absorption at 490 cm\(^{-1}\) indicated the presence of Cu-N bond [13]. In the complex \([\text{Cu}(\text{L}_5)_2\text{Cl}_2], \text{L}_5=(\text{E})-1-(\text{2-amino hydroxy benzylidene})\text{ quinoline}-2(1\text{H})\text{-one})\) also indicate the presence of Cu-N bond in the absorption at 471 cm\(^{-1}\) [14].

### Table 3. Infrared absorption of ranitidine hydrochloride and the complex

| Compounds | IR absorption (cm\(^{-1}\)) |
|-----------|-----------------------------|
|           | (C=N) | (C=C) | (N-H) | (Cu-N) |
| 2-amino-3-methylpyridine | 1583  | 1472  | 3193  | -      |
| [Cu(2-amino-3-methyl-pyridine)_4] SO_4\cdot4H_2O | 1649  | 1479  | 3187  | 475    |
|           | 1460  | 3157  |       |        |

3.6. Magnetic properties (μ\(_{eff}\))
The μ\(_{eff}\) value measured for the present Cu(II) complex is 1.85 B.M., this value shows that the complex is paramagnetic which has one unpaired electron BM [15]. The square planar complex of Cu(II) showed magnetic moment BM 1.81 to 1.86 BM [16-17], indicated that [Cu(2-amino-3-methyl-pyridine)_4]SO_4\cdot4H_2O was present in square planar geometry. Based on the above results, the structure in figure 3 is suggested for the complex.
Figure 3. Suggested structure of [Cu(2-amino-3-methylpyridine)$_4$]SO$_4$·4H$_2$O

4. Conclusion
The complex [Cu(2-amino-3-methylpyridine)$_4$]SO$_4$·4H$_2$O was able to be synthesized by mixing a methanolic solution of Cu(II) and a methanolic solution of 2-amino-3-methylpyridine solution with a mole ratio of 1:6 and stirring for 3 hours. The functional group coordinated to the Cu(II) was possibly N-pyridine, forming square planar geometry. The complex is paramagnetic has one peak at maximum UV-Vis absorption of 730 nm.

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References
[1] Islam I, Hossain A, Shah N, Barua H T, Kabir A, Khan M J, Mullick R 2015 Journal of Chemistry 2015 1-8
[2] Abu-Youssef M A M, Solimana S M, Langerb V, Goharc Y M, Hasanena A A, Makhyouna M A, Zakyd A H, and Öhrström L R 2010 Inorganic Chemistry 49 9788-9797
[3] Sharma N, Chaturvedi K 2014 International Journal of Current Microbiology and Applied Science 3(4) 65-74.
[4] Singh K, Thakur R, Kumar V. Journal of Basic and Applied Sciences 5 21–30
[5] Saleemh F A, Musameh S, Sawafa A, Brandao P, Tavares C J, Ferdov S, Barakat A, Al Ali, A, Al-Noaimi M, Warad I 2016 Arabian Journal of Chemistry, Article in Press
[6] Chimaine F T, Yufanyi D M, Yuoh A C B, Eni D B, Agwara M O 2016 Cogent Chemistry 2 1253905
[7] Rawat S P, Choudhary M 2014 International Journal of Inorganic Chemistry
[8] Todar K 2011 Staphylococcus aureus and Staphylococcal Disease (USA: Science Magazine)
[9] Fitriyana Nur 2012 Síntesis dan Karakterisasi Kompleks Cu(II) dengan Sepamet (Surakarta: Jurusan Kimia Fakultas Matematika dan Ilmu Pengetahuan Alam UNS)
[10] Onawumi O O Esther, I O Adeoye and F A Oluwafunmilayo Adegunde 2013 Open Journal of Inorganic Chemistry, vol. 3, hlm 26-33.
[11] Ababei L V, A Kriza, C Andronescu, A M Musuc 2011 Journal of the Serbian Chemical Society 2 1-24
[12] Suresh M S and V Prakash 2010 International Journal of the Physical Sciences 5(14) 2203-2211
[13] Anacona J R, Johan C, Ovidio A A 2013 Synthesis, Spectroscopic, and Magnetic Studies of Mono- and Polynuclear Schiff Base Metal Complexes Containing Salicylidene-Cefotaxime Ligand International Journal of Inorganic Chemistry Article ID 108740
[14] Al-Bayati R I H, Mahdi F R, Al-Amiery 2011 British Journal of Pharmacology and
Toxicology 2(1) 5-11

[15] Huheey E, James A, Keiter E and Keiter L R 1993 Inorganic Chemistry Fourth edition (New York: Harper Collins College Publisher)

[16] Raman N, Jeyamurugana R B, Rajkapoorb B, Mituc L 2010 J Iran Chem Soc 7(4) 917-933.

[17] Al-Shaalan N H 2011 Molecules 16 8629-8645