Synthesis and Elucidation Structure of *Tetrakis*-diphenylaminecopper(II) Chloride Hexahydrate

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Abstract. CuCl₂·2H₂O with diphenylamine formed a complex compound in 1:4-mole ratio of metal to the ligand in methanol. Its structural properties were investigated by employing metal content analysis by Atomic Absorption Spectroscopy (AAS), magnetic susceptibility, UV-vis and FTIR spectroscopy. The forming of the complex was indicated by shifting of UV-Vis spectra. The result of analysis Cu(II) in the complex showed empirical formula of the complex were Cu(diphenylamine)₂Cl₂(H₂O)₆. The electrical conductivity of complex showed the charge ratio of cation and anion = 2:1. Finally, the proposed formula of the complex was [Cu(diphenylamine)₂]Cl₂·6H₂O. Based on infrared spectra, it was revealed that diphenylamine existed as monodentate bind to copper(II) through the functional group of N-H. The electronic spectral study of the complex showed three transition peaks on 861, 592, and 419 nm corresponding to the ²B₁g → ²A₁g, ²B₁g → ²B₂g dan ²B₁g → ²E₂ transitions. The complex was paramagnetic and indicated that ligands form square planar geometry around the Cu(II).

1. Introduction

Copper complexes are able to form many geometries with different types and numbers of ligands. It is reported that copper complex forming square planar [1-3], tetrahedral [4-5], octahedral [6-8], trigonal planar [9-10], and square pyramidal [11-12] geometry. A large number of complexes have been synthesized. However, the various design of the copper complexes based on different ligands are still commonly interesting to learn among scientists. Each copper complex compound has unique chemical and physical properties.

Such compounds, particularly where the copper ion coordinately binds to organic molecules, play important roles in biological processes [13], e.g., blue copper protein and primarily associated with copper-dependent cellular enzymes [14]. Also, copper compounds are often used as a catalyst in industrial processes [15], in some cases allowing the production of material otherwise difficult to obtain, also being applied in the medicinal and pharmacological field [13],[16-17].

Diphenylamine is a chemical compound used as stabilizers in nitrocellulose-containing explosives and propellants. It is also used in the perfumery, as antioxidants in the rubber and elastomer industry, pharmaceuticals, the production of dyes, photography chemicals, and etc. [18]. Diphenylamine has a lone pair of electron on the nitrogen atom [19] as a donating site. Our attention is focused on ligands
containing N-H group during last years due to their coordination chemistry and ability to be an antibacterial agent [20-21].

The purpose of the present work is to report the data of the new complex of copper with diphenylamine ligand and its properties which are characterized by Atomic Absorption Spectroscopy (AAS), molar conductivity, UV-Visible, IR, and magnetic susceptibility measurements.

2. Experimental
2.1. Materials
All chemicals and solvents were of analytical grade and used as received without further purification. The metal salts (CuCl₂·2H₂O, CuSO₄·5H₂O, NiCl₂·6H₂O, NiSO₄·6H₂O, and AlCl₃·6H₂O) and diphenylamine were purchased from Merck.

2.2. Physical Measurements
The copper content was determined by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. Fourier transform infrared (FTIR) spectra of diphenylamine, CuCl₂·2H₂O, and its complexes as KBr pellets were recorded in the spectral range 4000–400 cm⁻¹ with a Perkin-Elmer Series 2000 apparatus. Molar conductivity (Λ*m) of 1 mM solution in methanol was measured on Jenway CE 4071 conductivity meter at 25 °C. Magnetic susceptibilities were measured on AUTO Sherwood Scientific 10169 Magnetic Susceptibility Balance (MSB) at room temperature. Spectra UV-VIS of metal complex and ligand was recorded in methanol solvent using Shimadzu UV-3601 spectrophotometer.

2.3. Synthesis of Cu(II) complex
The complex has been prepared by reaction of CuCl₂·2H₂O and diphenylamine in methanol. Methanolic solution (10 mL) of CuCl₂·2H₂O (0.341 g; 2 mmol) was added drop wise to methanolic solution (20 mL) of diphenylamine (1.354 g; 8 mmol) with constant stirring for 6 hours. The solution was then concentrated to 15 mL of volume and left to stand for 72 hours. The precipitate was filtered with filter paper and dried in a desiccator for 24 hours.

3. Result and Discussion
3.1. Electronic spectra
Figure 1 shows the shift of CuCl₂·2H₂O maximum absorption wavelength towards smaller wavelengths in the complex Cu(II)-diphenylamine. Shifting λₘₐₓ indicated the formation of the complex. It is due to the substitutions of H₂O molecules with diphenylamine and shows that diphenylamine has greater ligand field energy. Electronic spectra of the complex of Cu(II)-diphenylamine showed a wide absorption at λₘₐₓ 816, 592, and 419 nm assigned to the ²B₁g → ²A₁g, ²B₁g → ²B₂g, and ²B₁g → ²E₂g transition. It was reported that the three transitions attributed to square planar geometry such as in Cu-N-Nicotinoyl-N-o-hydroxythiobenzhydrazide [22]. However, the predicted geometry of the complex needs to confirm by other characterization methods.
3.2. Analysis of The Amount of Copper with Atomic Absorption Spectroscopy

The result of measurements of the copper content in complex was 6.91 ± 0.16 %. If the result of the measurement is compared with the copper content theoretically on various possible complex formulas, the formula can be approximated as Cu(diphenylamine)$_4$Cl$_2$·6H$_2$O.

3.3. Analysis of Electrical Conductivity

The molar conductivity of the complex was determined in methanol (10$^{-3}$ M) at room temperature. The molar conductance values of the complex lied in 33.96 ± 0.16 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 (shown in Table 1), it is seen that the charge ratio of cation:anion= 2:1. This fact showed that the chloride ions were not coordinated to the central metal ion Cu(II) and only act as an anion. The complex dissociates in solution to be [Cu(diphenylamine)$_4$]Cl$_2$ and 2 ions of Cl. Thus, it strengthened the proposed formula of the complex was probably [Cu(diphenylamine)$_4$]Cl$_2$·6H$_2$O.

**Table 1. Molar Conductivity of Metal Salts and Cu(II) complex in Methanol**

| Solution          | $\Lambda_\infty$ (S cm$^2$ mol$^{-1}$) | Cation : Anion Charge |
|-------------------|--------------------------------------|-----------------------|
| Methanol          | 1.04                                 | -                     |
| CuSO$_4$·5H$_2$O  | 8.60                                 | 1:1                   |
| NiSO$_4$·6H$_2$O  | 7.42                                 | 1:1                   |
| CuCl$_2$·2H$_2$O  | 47.16                                | 2:1                   |
| NiCl$_2$·4H$_2$O  | 53.16                                | 2:1                   |
| AlCl$_3$·6H$_2$O  | 90.96                                | 3:1                   |
| The complex       | 33.96 ± 0.16                         | 2:1                   |
3.4. Infrared Analysis

IR spectrum of Cu(diphenylamine)$_4$Cl$_2$-6H$_2$O showed a shift in the absorption of the aryl-NH-group toward a smaller wave number of 1319 cm$^{-1}$ (diphenylamine ligand) to 1313 cm$^{-1}$ Cu(diphenylamine)$_4$Cl$_2$-6H$_2$O which indicated that the cluster (aryl-NH-) ligands of diphenylamine are coordinated on Cu$^{2+}$ central ions. In the Cu(diphenylamine)$_4$Cl$_2$-6H$_2$O there was an uptake of the -OH broad group at 3396 cm$^{-1}$ which indicated the absorption of the O-H group of H$_2$O molecules, as occurs in complex [Zn(L)(L)${_2}$]3H$_2$O (L=2,6-pyridinedicarboxylate and L’ = 4,4’-dipyridylamine) showing widespread uptake in the 3400 cm$^{-1}$ region which is a water of crystalline dihydrate [23]. The absorption of clusters O-H broad from this H$_2$O molecule caused the absorption of the N-H group overlap, therefore, it did not appear. This is due to the nearly same region of the O-H and N-H infrared absorption [24].

3.5. Magnetic Properties ($\mu_{\text{eff}}$)

The $\mu_{\text{eff}}$ value measured for the present Cu(II) complex was 1.71 BM, which showed one unpaired electron, paramagnetic, and discrete magnetically non-coupled spin-only value for copper(II) ion. The magnetic moment value of Cu(II) complex indicated that [Cu(diphenylamine)$_4$]Cl$_2$-6H$_2$O is present in square planar geometry [25]. Based on the above results, the structure in Figure 2 is suggested for the complex.

![Figure 2. Suggested structure of [Cu(diphenylamine)$_4$]Cl$_2$-6H$_2$O](image)

4. Conclusion

The complex of [Cu(diphenylamine)$_4$]Cl$_2$-6H$_2$O, namely Tetrakis(diphenylamine) copper(II) chloride hexahydrate, was able to be synthesized by mixing methanolic solution of Cu(II) and methanolic solution of diphenylamine with a mole ratio of 1:4 and stirring for 6 hours. Electronic spectra of the complex showed a wide absorption at $\lambda_{\text{max}}$ 816, 592, and 419 nm assigned to the $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{1g} \rightarrow ^2B_{2g}$ dan $^2B_{1g} \rightarrow ^2E_{g}$ transition. The functional group coordinated to the Cu(II) was possibly N-H, forming square planar geometry. The complex was paramagnetic.

Acknowledgement

The authors gratefully express acknowledgments to Indonesian Ministry of Research Technology and Higher Education (RISTEKDIKTI) for financial support.

References

[1] Turkyilmaz M 2017 Journal of Thermal Analysis and Calorimetry 129(1) 451-460.
[2] Said M, Ahmad J, Rehman W, Badshah A, Khan H, Khan M, Rahim F and Spasyuk D
2015 *Inorganica Chimica Acta* 434 7-13.

[3] Dong Y, Dong X, Dong W, Zhang Y and Zhang L 2017 *Polyhedron* 123 305-315.

[4] Angel N, Khatib R, Jenkins J, Smith M, Rubalcava J, Le B, Lussier D, Chen Z, Tham F, Wilson E. and Eichler J 2017 *Journal of Inorganic Biochemistry* 166 12-25.

[5] Huang M, Guo Y, Shi Y, Zhao L, Niu Y, Shi Y and Li X 2017 *Inorganica Chimica Acta* 457 107-115

[6] Alabdali A *Journal of Applied Chemistry* 3 2 5-10.

[7] Bibi S, Mohamad S, Manan N, Ahmad J, Kamboh M, Khor S, Yamin B and Abdul Halim S 2017 *Journal of Molecular Structure* 1141 31-38.

[8] Olalekan T, Ogunlaja A, VanBrech B, and Watkins G 2016 *Journal of Molecular Structure* 1122 72-79.

[9] Alfonso S, González S, Higuera-Padilla A, Vidal A, Fernández M, Taylor P, Urdanibia I, Reiber A, Otero Y and Castro W 2016 *Inorganica Chimica Acta* 453 538-546.

[10] Khalaji A, Peyghoun S, Akbari A, Feizi N, Dusek M and Eigner V 2017 *Journal of Chemical Sciences* 128(6) 883-891.

[11] Routaray A, Nath N, Maharana T, Sahoo P, Das J and Sutar A 2016 *RSC Adv* 4(60) 32004-32012.

[12] Hu K, Li F, Zhang Z. and Liang F 2017 *New J. Chem.* 41(5) 2062-2072.

[13] Srivastava A N K, Singh, and SM Singh 2015 *International Journal of Environmental Science* 75 012025 doi :10.1088/1755-1315/75/1/012025

[14] Shrivastava A N K, Singh, and SM Singh 2015 *International Journal of Environmental Science* 75 012025 doi :10.1088/1755-1315/75/1/012025