Synthesis and Characterization of A Coordination Complex of Tetrakis(diphenylamine)copper(II) Sulfate Hexahydrate

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Abstract. CuSO₄·5H₂O with diphenylamine formed a complex compound in 1:4 mole ratio of metal to the ligand in methanol. The forming of the complex was indicated by shifting of UV-Vis spectra of CuSO₄·5H₂O and the complex from 819 nm to 593 nm. The result of analysis Cu(II) in the complex showed the copper content in the complex was 6.43 % therefore the empirical formula of the complex was Cu(diphenylamine)₂SO₄·(H₂O)₆. The electrical conductivity of complex showed the charge ratio of cation and anion = 1:1. Therefore, the proposed formula of the complex was [Cu(diphenylamine)₂]SO₄·6H₂O. Based on infrared spectra, it was determined that the functional group of N-H of diphenylamine was coordinated to the center ion Cu²⁺. The electronic spectral study of the complex showed a transition peak on λ = 593 nm (υ = 16863 cm⁻¹) corresponding to the 2B₁g → 2A₁g transition. The complex was paramagnetic with effective magnetic moment 1.72 B.M. It was indicated square planar geometry around Cu(II).

1. Introduction
The coordination chemistry of copper plays an important role in many fields. Synthesized copper complex has been reported to have a potentiality in catalytic system [1-2], solar cell as dye sensitizer [3-4], antibacterial [5-6], antifungal [7-9], anticancer [10-11], and etc. Copper complexes are able to form many geometries with different types and numbers of ligands. It is reported that copper complex forming square planar [12-14], octahedral [15-16], tetrahedron [17-18], trigonal planar [18-19], and square pyramidal [13,20] geometry. Although a large number of complexes have been obtained, the synthesis and design of novel copper complexes by varying the nature of the reactants and synthetic conditions are still under investigation.

Diphenylamine is an organic compound with the formula (C₆H₅)₂NH, colorless solid but often yellow due to oxidized impurities [21]. Diphenylamine and its derivatives are commonly used as stabilizers in nitrocellulose-containing explosives and propellants, in the perfumery, and as antioxidants in the rubber and elastomer industry, also widely used for the production of dyes, pharmaceuticals, photography chemicals and further smallscale application [22]. Diphenylamine is a monodentate ligand as well, having one donating site with a lone pair of electron on the nitrogen atom [21]. Besides, our attention is focused on ligands containing N-H group during last years. The ligands have been interesting compounds because of their coordination chemistry and ability to be an antibacterial agent.
In this work, we report the new complex of copper with diphenylamine ligand. The Cu(II) complex has been characterized through 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, AlCl₃·6H₂O) and diphenylamine were purchased from Merck.

2.2. Physical Measurements
The copper content was determined by Atomic Absorption Spectrophotometer (AAS) Shimadzu AA-6650. Infrared spectra were recorded on Prestige-21 Shimadzu spectrophotometers as KBr pellets in the frequency range of 4000–450 cm⁻¹. Molar conductivity (Λ*m) of 1 mM solution in methanol was measured on Jenway CE 4071 conductivity meter at 25 °C. The magnetic moment was measured using Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance. 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 CuSO₄·5H₂O and diphenylamine in methanol. Methanolic solution (10 mL) of CuSO₄·5H₂O (0.748 g; 3 mmol) was added dropwise to methanolic solution (20 mL) of diphenylamine (2.031 g; 12 mmol) with constant stirring for 6 hours. The solution was then concentrated to 15 mL of volume and left to stand for 48 hours. The precipitate was filtered with filter paper, then dried in a desiccator for 24 hours.

3. Result and Discussion
3.1. Electronic spectra
Figure 1 shows the shift of CuSO₄·5H₂O maximum absorption wavelength (819 nm) towards smaller wavelengths in the complex Cu(II)-diphenylamine (593 nm). Shifting λmax indicates the formation of the complex due to the substitutions of H₂O molecules with diphenylamine. It was estimated that diphenylamine acting as a stronger ligand than H₂O. Electronic spectra of the complex Cu(II)-diphenylamine show a wide absorption at λmax 593 nm (16863 cm⁻¹) assigned to the 2B₁g → 2A₁g transition. It was reported that the maximum wavelength of copper complexes in 613 [23], 586 [24], or 579 [24] nm attributed to square planar geometry.

![Figure 1. Electronic spectra of CuSO₄·5H₂O solution (a) and the complex solution (b)]
3.2. Analysis of the Amount of Copper with Atomic Absorption Spectroscopy
The results of measurements of the copper content in complex CuSO$_4$·5H$_2$O with diphenylamine was $6.43 \pm 0.16\%$. If the results of these measurements as compared with the levels of copper are theoretically on the various possibilities of complex formulas, then the formula can be approximated complex CuSO$_4$·5H$_2$O with diphenylamine which most likely is Cu(diphenylamine)$_4$SO$_4$·6H$_2$O. It needs more methods to confirm the number of presence of water molecules, such as thermogravimetry and differential thermal analysis.

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 lie in $13.39 \pm 0.10$ 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 is 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 [25]. The complex dissociates in solution to be [Cu(diphenylamine)$_4$]$^{2+}$ and SO$_4^{2-}$. Thus, it strengthens the proposed formula of the complex is probably [Cu(diphenylamine)$_4$]SO$_4$·6H$_2$O namely Tetrakis(diphenylamine)copper(II) sulfate hexahydrate.

3.4. Infrared Analysis
In the infrared spectra, shown in Figure 2 and Figure 3, the secondary N-H vibration of the ligand (3406 and 3383 cm$^{-1}$) was shifted to lower frequencies (3404 dan 3381 cm$^{-1}$) upon complex formation revealing coordination of the amine nitrogen atom. The aryl-NH vibration of the ligand (1319 cm$^{-1}$) is shifted to lower frequencies as well (1317 cm$^{-1}$). No absorption band of -OH was noticed due to overlapping of the N-H and –OH absorption band.

![Figure 2. Infared spectra of diphenylamine](image-url)
3.5. Magnetic Properties ($\mu_{\text{eff}}$)

The $\mu_{\text{eff}}$ value measured for the present Cu(II) complex is 1.72 BM which has one unpaired electron B.M. [26] and discrete magnetically non-coupled spin-only value for copper(II) ion [27]. The magnetic moment value of Cu(II) complex indicates that $[\text{Cu(diphenylamine)}_4]\text{SO}_4\cdot6\text{H}_2\text{O}$ is present in square planar geometry [26],[28]. The copper complex was formed by coordination of four N-H groups of diphenylamine. Each atom will produce the same strength of repulsion. The distance and position of each atom will be the same to achieve the least possible repercussion [29]. Based on the above results, the structure shown in Figure 4 is suggested for the complex.

![Figure 3. Infrared spectra of the Cu(II) complex](image)

![Figure 4. Suggested structure of $[\text{Cu(diphenylamine)}_4]\text{SO}_4\cdot6\text{H}_2\text{O}$](image)

4. Conclusion

The complex $[\text{Cu(diphenylamine)}_4]\text{SO}_4\cdot6\text{H}_2\text{O}$ was able to be synthesized by mixing a methanolic solution of Cu(II) in and a methanolic solution of diphenylamine solution with a mole ratio of 1:4 and
stirring for 6 hours. The complex was paramagnetic. The functional group coordinated to the Cu(II) was possibly N-H, forming square planar geometry.

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