Synthesis and Structure Characterization of Copper(II) Complex with Phenylhydrazine

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Abstract. The Cu(II)-phenylhydrazine complex was synthesized and characterized by ultraviolet-visible spectroscopy, atomic absorption spectroscopy, thermogravimetry/differential scanning calorimetry, molar conductivity, infrared spectroscopy and magnetic susceptibility measurements. The metal complex was prepared through reaction of 1:4 mole ratio of CuSO\(_4\).5H\(_2\)O to phenylhydrazine ligand in methanol at room temperature for 15 minutes. The peak shifting in the electronic spectra to the smaller maximum wavelength than copper salt from 815 nm to 518 nm indicated the formation of the complex. The copper content in the complex was 13.93\% which was according to the empirical formula of Cu(phenylhydrazine)\(_2\)(SO\(_4\))(H\(_2\)O)\(_n\) (n = 4, 5, or 6). Thermal analysis showed the release of five water molecules as hydrate and the electrical conductivity showed that the complex was non-electrolyte. The complex was paramagnetic with an effective magnetic moment of 1.93 BM. The broadness band peak of the electronic spectra at 19531 cm\(^{-1}\) showed the d-d transition. The studies confirmed that the ligand is monodentate and the proposed formula of the complex was [Cu(phenylhydrazine)\(_2\)(SO\(_4\))]\(\cdot\)5H\(_2\)O with square planar geometry.

1. Introduction
Coordination chemistry has become an interesting research topic in recent decades because it involves various ligands that have different functional groups and coordinate modes with metal ions [1], which provide different geometries with typical properties, new reactivity, and various applications [2]. Several of transition metal complexes, especially the 3d metal, exhibit diversity of biological activities including antimicrobial, antioxidant, anti-inflammatory, and anticancer properties [3-6] due to their low toxicity and high permeability in the cell membrane microorganism [7]. The copper (II) coordination chemistry is attracting a lot of attention due to its stable properties, diverse geometries and biological relevance [8-9]. Copper (II) as the d\(^8\) center metal with borderline softness is suitable for imine and amine ligands such as hydrazine which can form a square planar, distorted square planar, trigonal pyramid, square pyramidal or distorted octahedral geometry [9].

Phenyldiazine is derivatives of hydrazine which is widely applied in the medical field, because it contains amine nitrogen and also aromatic which gives a good pharmacological effect [10-11]. The lone pair electrons of the secondary amine nitrogen atom make hydrazine and its derivatives can act as ligand and produce metal complexes [12-13]. It has been previously investigated that copper complex...
with hydrazine derivative provides better biological activity compared to free ligand [14]. Therefore, it is very interesting to explore the coordination mode with biologically active ligands such as phenylhydrazine.

In this work, the synthesis and structural formation of copper complex with phenylhydrazine was studied using several techniques such as UV-Visible, Atomic Absorption Spectroscopy (AAS), molar conductance, Thermogravimetry/ Differential Scanning Calorimetry (TG/DSC), Infrared spectroscopy, and magnetic susceptibility measurements.

2. Experimental
2.1. Materials
All of the chemicals and solvents used for the synthesis were analytical grade and used as received without further purification. All chemicals such as Methanol, Ethanol, Dimethyl Sulfoxide (DMSO), CuSO$_4$·5H$_2$O, NiCl$_2$·6H$_2$O, CuCl$_2$·6H$_2$O, CoCl$_2$·6H$_2$O, FeSO$_4$·7H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O, and phenylhydrazine were E. Merck products.

2.2. Physical measurements
The electronic spectra (UV-Vis spectra) of CuSO$_4$·5H$_2$O and the metal complex was put on record in ethanol solvent using UV-Vis Double Beam Lambda 25 Perkin Elmer spectrophotometer. The copper content was determined by Atomic Absorption Spectroscopy (AAS) Shimadzu AA-6650. Molar conductivity was measured on conductivity meter Jenway CE-4071. The thermal analysis (TG-DSC) was performed through Diamond STA Linseis PT-1600 under heating rate of 80 °C/minute. IR spectrums of phenylhydrazine ligand and the copper complex were recorded on Prestige-21 Shimadzu spectrophotometers. The effective magnetic moment ($\mu_{\text{eff}}$) was measured by Magnetic Susceptibility Balance (MSB) Auto Sherwood Scientific 10169.

2.3. Synthesis of Cu(II) complex
Phenylhydrazine (0.216 g, 2 mmol) in 5 mL of methanol solvent was added dropwise to a methanolic solution (5 mL) of copper sulphate pentahydrate (0.249 g, 0.5 mmol) accompanied by a stirring continuously for 15 minutes at room temperature. Then, the blackish green precipitated was filtered off, washed with methanol and dried under vacuum (0.164 g, 70.42%).

3. Result and Discussion
3.1. Formation of the complex
Formation of Cu(II)-phenylhydrazine complex can be signified by the maximum wavelength shifting of Cu(II) solution in ethanol towards the lower wavelength, which can be seen in Figure 1. The maximum wavelengths shifted from 815 nm (CuSO$_4$·6H$_2$O) toward smaller wavelengths of 518 nm in the Cu(II)-phenylhydrazine complex. This shifting reveals that phenylhydrazine has stronger ligand field energy than H$_2$O [15]. So that phenylhydrazine can replace the position of water as coordinated molecules to copper ion in ethanol.
Figure 1. Electronic spectra of (a) CuSO₄·5H₂O (b) Cu(II)-phenylhydrazine complex in ethanol

3.2. Copper content analysis with Atomic Absorption Spectroscopy

The result of copper content measurement in the Cu(II)-phenylhydrazine complex was 13.91 ± 0.23%. Formula of the complex can be determined by comparing the experimental result of copper content in the complex with theoretical copper content that correspond to the various possible complex formulas shown in Table 1. Therefore, it can be approximated that the empirical formula of the complex is Cu(phenylhydrazine)₂SO₄·5H₂O (n= 4, 5, and 6).

| Empirical Formula | Mr (g/mol) | Copper content (%) |
|-------------------|------------|--------------------|
| Cu(phenylhydrazine)₂(SO₄)(H₂O)₄ | 447.78 | 14.18 |
| Cu(phenylhydrazine)₂(SO₄)(H₂O)₅ | 465.78 | 13.63 |
| Cu(phenylhydrazine)₂(SO₄)(H₂O)₆ | 483.78 | 13.12 |

3.3. Thermal analysis

Thermal analysis of the complex was carried out by TG-DSC for estimating the water molecules existence. The thermogram of the complex (Figure 2) exhibited that the complex is stable up to 79 °C and start decomposing in the TGA curve accompanied by an endothermic peak (DSC curve) at 104 °C in the temperature range of 55-131 °C. Then, the reduction of compound mass of 18.54% occurred at that range of temperature, which is equivalent to the release of five water molecules. Such a low temperature (>150 °C) decomposition and endothermic dehydration show that the water molecules are not coordinated to the center metal ion or as hydrate in the complex [13, 16]. Therefore, the estimated formula of the complex is Cu(phenylhydrazine)₂SO₄·5H₂O.
3.4. Molar conductivity analysis

The molar conductivity measurement was applied to found out the conductivity of the complex and its cation-anion charge ratio. Besides, the position of sulphate ion in the complex was also confirmed by comparing the molar conductivity of the copper(II) complex to the molar conductivity of the standard solutions of known metal salts (in DMSO 10⁻³ M), shown in Table 2. The molar conductivity of Cu(II) complex was 0 S.cm⁻².mol⁻¹, which showed that the complex was non-electrolyte [17]. This indicates the absence of counter ions in the Cu(II)-phenylhydrazine complex so that the sulphate ion is also coordinated to the Cu(II) center ion. Thus, the proposed complex formula of Cu(II)-phenylhydrazine was [Cu(phenylhydrazine)₂(SO₄)]·5H₂O.

Table 2. Molar conductivity of metal salts standard and Cu(II) complex in DMSO

| Solution          | Λ_M (S.cm².mol⁻¹) | Cation: Anion Charge |
|-------------------|-------------------|----------------------|
| DMSO              | 0                 | -                    |
| CuSO₄·5H₂O        | 2                 | 1:1                  |
| FeSO₄·7H₂O        | 2                 | 1:1                  |
| CuCl₂·6H₂O        | 11                | 2:1                  |
| CoCl₂·6H₂O        | 21                | 2:1                  |
| NiCl₂·6H₂O        | 28                | 2:1                  |
| Fe(NO₃)₃·9H₂O     | 61                | 3:1                  |
| Cu(II)-phenylhydrazine | 0               | -                    |

3.5. Electronic spectra and magnetic studies

The electronic spectra of the Cu(II) complex (Figure 2) exhibited the characteristic band at 19286 cm⁻¹ (518 nm) with a molar absorptivity of 730.5 L/mol.cm. This single band in visible corresponds to the d-d transition [18], which is a combination from the three transitions band allowed of ²B₁g→²A₁g, ²B₁g→²B₂g, and ²B₁g→²Eg. It is due to the little energy difference between those bands, so it is hard to separate them into several bands and observe them [16]. The d-d transition bands in the octahedral and tetrahedral complexes appear in the region of 800 nm and 1200 nm, respectively [19]. Meanwhile, the

![Figure 2. Thermogram of Cu(II)-phenylhydrazine complex](image-url)
The Jahn Teller effect can happen in the octahedral field and induce the large blue-shift in the range under 700 nm, which is reported for the square planar geometry [20-22].

The effective magnetic moment ($\mu_{\text{eff}}$) value of the Cu(II) complex was 1.93 ± 0.02 BM. The copper(II) complex possess $\mu_{\text{eff}}$ within the range of 1.63-2.15 BM, indicating that the complex was paramagnetic, in which the copper(II) ion is in the d$^9$ system with single unpaired electron. And this also shows that the complex has a square planar structure [23] and does not have Cu-Cu bonding. Whereas the Cu-Cu bonding has a smaller magnetic moment value than the spin only magnetic moment value ($\mu_c$; 1.73 BM) [18] due to the unpaired electrons are paired when bonding one another. Therefore, the Cu(II)-phenylhydrazine complex was predicted to form square planar geometry.

3.6. Infrared analysis

The IR absorption bands provide information about the coordination mode in the complex through the functional groups, where the main bands of the ligand and its copper complex IR spectra are presented in Table 3. The IR spectra of the copper complex showed a shift in absorption bands at 3244 and 3090 cm$^{-1}$ as compared to the free ligand (3331 and 3093 cm$^{-1}$), and these bands can be attributed to two pairs of stretching and bending of $\nu$(N-H) [24-25], where the shift exhibits the coordinated amine group. Besides, the shifting of $\nu$(N-N) band in the complex becomes 981 cm$^{-1}$ also revealed that the ligand coordinates to the metal center through the nitrogen amine group [26].

The additional absorbance band appeared on the IR spectra of the complex at 1206, 1141, 1092, and 868 cm$^{-1}$ correspond to sulphate ion (SO$_4^{2-}$). Where the bands indicates the complex formation of chelating bidentate with coordination to one metal ion through two oxygen of sulphate ion [26], which are attributed to the asymmetric and symmetric stretching of S=O and S-O band [27]. By considering the copper complex which has a coordination number of four, in which two oxygen atoms of sulphate ion have been donated for coordinating to the metal ion so that the phenylhydrazine ligand acts as a monodentate ligand, which only contributes one of its nitrogen atoms. And the most possible is the nitrogen of primary amine, due to its less steric hindrance than the secondary amine.

The presence of additional bands in the 486 and 451 cm$^{-1}$ regions corresponding to Cu-N and Cu-O vibrations, respectively [19, 28], although they appear in adjacent regions. Due to sometimes multiple metal-ligand stretching frequencies arise in overlapping regions [19]. Hence, it strengthens the complex coordination mode via oxygen and nitrogen atoms so the proposed structure was shown in Figure 3.

Table 3. Infrared Absorption of phenylhydrazine and the Cu(II) complex

| Functional Group | Infrared Absorption (cm$^{-1}$) |
|------------------|----------------------------------|
| Phenylhydrazine  | Cu(II) Complex                   |
| $\nu$(-NH/-NH$_2$)| 3331 and 3093                    |
| $\nu$(N-N)       | 1073                             |
| $\nu$(SO$_4^{2-}$)| -                               |
| $\nu$(OH) (water molecule) | -               |
| $\nu$(Cu-N)      | -                               |
| $\nu$(Cu-O)      | -                               |
4. Conclusion

The copper complex derived from phenylhydrazine was successfully synthesized by stirring CuSO$_4$·5H$_2$O and phenylhydrazine in methanol for 15 minutes at room temperature with a 1:4 mole ratio of metal to the ligand. Further, the complex has been structurally characterized so the proposed formula of the complex was [Cu(phenylhydrazine)$_2$(SO$_4$)]·5H$_2$O. The phenylhydrazine was a monodentate ligand, in which the primary amine nitrogen as a functional group was coordinated to the copper ion. Meanwhile, the sulphate ion act as a bidentate ligand through its two oxygen atoms coordinated to center ion and forming a square planar complex. The complex properties were non-electrolyte and paramagnetic.

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