Synthesis and characterization of bis-(2-cyano-1-methyl-3-{2-\{(5-methylimidazol-4-yl)methyl\}thio}ethyl)guanidine copper(II) sulfate tetrahydrate

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Abstract. Complex of copper(II) with 2-cyano-1-methyl-3-{2-\{(5-methylimidazol-4-yl)methyl\}thio}ethyl)guanidin(xepamet) had been synthesized in 1 : 4 mole ratio of metal to the ligand in methanol. The complex was characterized by metal analysis, thermal gravimetry/differential thermal analyzer (TG/DTA), molar conductivity meter, (Fourier transform infrared spectroscopy) FT-IR, UV-Vis spectroscopy, and magnetic susceptibility balance. The molar conductivity measurement shows that the complex was 2: 1 for electrolyte and SO\textsubscript{4}\textsuperscript{2-} which was acting as a counter ion. The thermal analysis by Thermogravimetric (TG) indicates that the complex contained four molecules of H\textsubscript{2}O. The Infrared spectral data indicates that functional groups of (C=N) imidazole and (C-S) are coordinated to the center ion Cu\textsuperscript{2+}. Magnetic moment measurement shows that the complex is paramagnetic with \(\mu_{\text{eff}} = 1.78 \pm 0.01\) BM. Electronic spectra of the complex show a broad band at 608 nm (16447.23 cm\textsuperscript{-1}) are due to Eg\textsubscript{\textsuperscript{→}}T\textsubscript{2g} transition. Based on those of characteristics, The complex formula was estimated as [Cu(xepamet\textsubscript{2})\textsubscript{SO\textsubscript{4}}\textsubscript{4H\textsubscript{2}O}. The structure of [Cu(xepamet\textsubscript{2})\textsubscript{SO\textsubscript{4}}\textsubscript{4H\textsubscript{2}O complex is probably square planar.

1. Introduction

Recently, the research field in solar energy has been studied and widely developed. Some studies are focusing on a photocatalytic system using TiO\textsubscript{2} [1]. However, TiO\textsubscript{2} possesses ultraviolet absorbance, while the solar light energy possesses wider range absorbance. To enhance the sensitivity of TiO\textsubscript{2} in the wider range, the addition of other substances that have visible area absorbance is required. Dyes are one of the substances that can be added to modify the UV absorbance-possessed material due to their optical properties in visible area absorbance. Organic dyes are usually made of chlorophyll and coumarin. However, these organic substances are vulnerable to high temperature [2]. Other substance such complex compounds might be able to be used as a sensitizer that not vulnerable to high temperature and able to absorb visible light.

Complex compounds that absorb visible light area are mainly colored transitional metal ion complexes, for example, complexes of copper. Copper (II), has visible light area absorbance ranging from 600 nm – 820 nm. The maximum of absorbed wavelength depends on the ligands bonded to the complexes [3]. The ligands also determine the geometry complex [4]. The complexes of copper (II) are generally high in stability compared to that of the first periodic transitional metal.

The Cu (II) complex can create many geometries depending on the bonded ligands. For example complex Cu[[N,N’-bis(3,5-di-t-pentylsalicyliden)-1,2-ettlendiamin]-N,N’,O,O’] has a flat rectangular
geometry, of which two nitrogen atoms (C=N) and two O atoms ligand \(N,N'-\text{bis}(3,5-\text{di-t-pentylsalicylidene})\) are coordinated to the central ion Cu(II) tetradentately [5]. Complex Cu[(3-O\(_2\)Nbz)\(_2\)(nia)(H\(_2\)O)\(_2\)] (nia=nicotinamid, 3-O\(_2\)Nbz = 3-nitrobenzoate) has a square pyramidal geometry, of which two molecules 3-nitrobenzoate are coordinated by two O atoms, while nicotinamide by cyclic atom N is coordinated to the central ion Cu(II) monodentately [6]. Complex \([M(L^1)SO_4], M = \text{Co(II)}, \text{Ni(II)} \text{and Cu(II)}, L^1 = 3,3'-\text{thiodiopropionic-acid-bis(4-amino-5-ethylimino-2,3-dimethyl-1-phenyl-3-pyrazoline)},\) has a octahedral geometry. \(L^1\) is coordinated to the metal ion Penta dentately by two azomethine nitrogen atoms, two groups of NH and one atom of sulfur (C-S) [7]. Complex [(BPCA)Cu(MA)] (\(MA = \text{racemic mandelate, BPCA=bis(2-pyridylcarbonyl)amidate}\)) has distorted square pyramid geometry; ligand MA is coordinated by atom O while BPCA is coordinated by two groups of (C=N) and one (N-H) trientately [4]. Complex \([M(CA)_2(Ad)X_2], M = \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}, \text{Cd(II)}, \text{and Cu(II)}, \text{CA=} \text{caffein, Ad=} \text{adenine and X = SCN{}}\) show how caffeine is coordinated to metal ions monodentately by atom nitrogen group (C=N), while adenine is coordinated bidentately by atom nitrogen group (C=N). Two thiocyanate ions are coordinated to the metal ions by sulfur atoms. This coordination results in octahedral geometry complexes [8].

The examples of complexes explained above reveals how various groups (C=N), (C-S), (N-H) that are coordinated to the central ion Cu(II) result in complex Cu(II) with various flat rectangular, tetragonal pyramidal or octahedral geometry, coordinated mono dentately or chelatedly. One of the ligand compounds containing groups (C=N), (C-S), (N-H) and (C≡N) coincidently is xepamet, of which the structure is shown in figure 1. Hence, many possibilities of complex structure Cu(II)-xepamet may be formed. Therefore, here we report the synthesis and characterization of a complex of Cu(II)-xepamet which was successfully synthesized and investigated to its potential for solar cell application.

![Figure 1. Structure of Xepamet](image)

2. Experimental

All chemicals were purchased from E.Merck and used without further purification. The IR spectra were recorded on a Spectrophotometers Prestige-21 Shimadzu. The copper content was determined by Atomic Absorption Spectrometer (AAS) Shimadzu AA-6650. The thermogravimetric analysis of the metal complex was performed by a TG/DTA Diamond Perkin Elmer analyzer. Spectra UV-VIS was performed with a Shimadzu UV-3601 spectrophotometer. Molar conductivity (\(\Lambda^*\)) of 1 mM solution in water was measured at 25 °C with a Jenway CE 4071 Conductivity meter. The magnetic moment was measured with Auto Sherwood Scientific 10169 Magnetic Susceptibility Balance.

2.1. Determination of Coordinated Numbers of Cu(II)

Coordinated numbers for Cu(II) complex with xepamet were determined by the comparison method of metal moles and ligand moles. This methodology was exercised by creating a solution of CuSO\(_4\).5H\(_2\)O and xepamet. The comparisons between mole of CuSO\(_4\).5H\(_2\)O and mole of xepamet are 1:0, 1:1, 1:2, 1:3, 1:4, 1:5, 1:6. Each solution was measured using UV-Vis spectrophotometers to obtain maximum wavelength (\(\lambda_{\text{max}}\)). A graphic was then made comparing maximum wavelength as an ordinate and the comparison between ligand mole and metal mole as the abscissa. By using the graphic, it was then determined the comparison between the amount of moles of the metal ions and the ligands in the
complexes on the equal basis. The mixture composition of CuSO\(_4\).5H\(_2\)O and xepamet in methanol are given in Table 1.

| No. | Comparison of mmol CuSO\(_4\).5H\(_2\)O and xepamet | Cu\(^{2+}\) (mmol) | Cu\(^{2+}\) (mg) | xepamet (mmol) | xepamet (mg) |
|-----|----------------------------------------------------|-------------------|-----------------|----------------|--------------|
| 1.  | 1:0                                                | 0.1               | 25              | 0              | 0            |
| 2.  | 1:1                                                | 0.1               | 25              | 0.1            | 25.2         |
| 3.  | 1:2                                                | 0.1               | 25              | 0.2            | 50.4         |
| 4.  | 1:3                                                | 0.1               | 25              | 0.3            | 75.6         |
| 5.  | 1:4                                                | 0.1               | 25              | 0.4            | 100.8        |
| 6.  | 1:5                                                | 0.1               | 25              | 0.5            | 126.0        |
| 7.  | 1:6                                                | 0.1               | 25              | 0.6            | 151.2        |

2.2. Complex Synthesis

A solution of copper(II) sulfate pentahydrate (0.249 g, 1 mmol) in methanol (15 mL) was added to a hot solution of the ligand (1.009 g, 4 mmol) in methanol (30 mL) and the resulting solution was refluxed for 1 h. The volume was reduced to half and left for about 24 hours. The green precipitate, which formed was separated, washed with methanol and dried under vacuum.

3. Results and Discussion

3.1. Determination of Coordinated Numbers of Cu (II)

The result of spectra of the determined coordinated numbers of Cu(II) and xepamet is shown in Figure 2 while the graphic \(\lambda_{\text{max}}\) versus comparison of mol CuSO\(_4\).5H\(_2\)O and xepamet is shown in Figure 3.

![Figure 2](image-url)  
**Figure 2.** The spectra of complexes of Cu(II)-xepamet with various mole ratios.
Figure 3. Graphic $\lambda_{\text{max}}$ versus the comparison of moles of CuSO$_4$.5H$_2$O and xepamet.

Figure 3 shows a friction of $\lambda_{\text{max}}$ absorbance of solution mixture Cu(II) and xepamet. The graphic depicts how the value of $\lambda_{\text{max}}$ comparison of mol Cu (II) and xepamet by 1:2 is in the constant value, suggesting the complex was successfully formed by the comparison of mol Cu(II) and xepamet by 1:2.

3.2. Complex Synthesis

The mixture of CuSO$_4$.5H$_2$O (0.249 g) solution in methanol (15 mL) and solution of xepamet (1.009) in hot methanol (30 mL) creates a green crystal. The electronic spectrum can be seen in figure 4.

Figure 4. Electronic spectrum (a) solution of CuSO$_4$.5H$_2$O and (b) solution of complex Cu(II)-xepamet within the water.
Figure 4 shows a shift of maximum wavelength absorbance of CuSO$_4$.5H$_2$O (806 nm) to a smaller wavelength (608 nm) in the complex Cu(II)-xepamet. The shift of $\lambda_{\text{max}}$ reveals the formation of complexes between Cu(II) and xepamet and also reveals that xepamet is a stronger ligand than H$_2$O.

3.3. Determination of Formula and Characteristics of Complexes

The measurements of the amount of Cu in the complexes of Cu(II)-xepamet are of 8.71±0.24%. If the result of the measurement is compared to the theoretical amount of Cu (8.62%), the estimated complex compound formula for Cu(II)-xepamet is possibly Cu(xepamet)$_2$.SO$_4$.4H$_2$O.

3.4. Thermal Analysis with TG/DTA

TG/DTA analysis for Cu(II)-xepamet complex is shown in figure 5. Figure 5 shows that the complexes are decomposed through several levels. The TG curve of Cu(II)-xepamet complex depicts the reduction of 9.5% of the mass in the first level at 79.9-146.4 °C, indicating the release of four molecules of H$_2$O (of which the theory is 9.78%). This is supported by the appear of the endothermal peak at 105 °C on the DTA curve. The next level shows two peaks approximately at 180 °C and 260 °C. In this level, mass reduction is hardly seen. The TG/DTA analysis supports Cu(xepamet)$_2$.SO$_4$.4H$_2$O complex formula.

Figure 5. Analysis of DTA (a) and TG (b) of Cu(II)-xepamet complex.
3.5. Electrolytic Conductivity Measurement

The Electrolytic Conductivity Measurement is shown in table 2. The electrolytic conductivity of complex \( \text{Cu(xepamet)}_2\text{SO}_4\cdot\text{H}_2\text{O} \) is similar to copper(II) sulfate and nickel(II) sulfate indicates that the complex is an electrolyte corresponds to 1 : 1 electrolyte. Sulfate is a counter ion and not coordinate to Cu(II) as in \([\text{Cu(INHCBA)}_2(\text{H}_2\text{O})_2](\text{SO}_4)\cdot\text{H}_2\text{O}, \text{INHCBA} = \text{isonicotinamido-4-chlorobenzalaldimine} \) complex [9]. Therefore, these complexes may be formulated as \([\text{Cu(xepamet)}_2]\text{SO}_4\cdot\text{H}_2\text{O} \).

Tabel 2. The Electrolytic conductivity of standar solution and complex \( \text{Cu(xepamet)}_2\text{SO}_4\cdot\text{H}_2\text{O} \pm 1.10^{-3} \text{ M in water} \)

| Solution            | \( \Lambda_m^* \) (S.cm\(^2\).mol\(^{-1}\)) | Number of ions |
|---------------------|---------------------------------------------|----------------|
| CuSO\(_4\cdot\text{H}_2\text{O} \) | 144.2 ± 0.2                                | 2              |
| NiSO\(_4\cdot\text{H}_2\text{O} \) | 162.4 ± 0.2                                | 2              |
| CuCl\(_2\cdot\text{H}_2\text{O} \) | 235.7 ± 1.0                                | 3              |
| NiCl\(_2\cdot\text{H}_2\text{O} \) | 257.7 ± 1.0                                | 3              |
| AlCl\(_3\cdot\text{H}_2\text{O} \) | 349.7 ± 1.0                                | 4              |
| Cu(xepamet)_2\text{SO}_4\cdot\text{H}_2\text{O} | 133.2 ± 0.3                              | 2              |

3.6. Infra-Red Spectra

The infrared spectra of xepamet and complex \([\text{Cu(xepamet)}_2]\text{SO}_4\cdot\text{H}_2\text{O} \) are shown in figures 6 and 7, while IR absorption bands are shown in table 3.

\[ \nu(\text{C=O}) \quad 2177.63 \text{ cm}^{-1} \]
\[ \nu(\text{C=S}) \quad 636.66 \text{ cm}^{-1} \]
\[ \nu(\text{N-H}) \quad 3224.98 \quad \text{and} \quad 3141.04 \text{ cm}^{-1} \]
\[ \nu(\text{C=S}) \quad 1078.28 \text{ cm}^{-1} \]
\[ \nu(\text{C=N}) \quad 1622.28 \quad \text{and} \quad 1587.42 \text{ cm}^{-1} \]

Figure 6. The infrared spectra of xepamet.
The IR spectrum of the complex $\text{[Cu(xepamet)\textsubscript{2}]SO\textsubscript{4}.4H\textsubscript{2}O}$ in the 1604.77; 1585.49; 1053.58; 607.58 cm\(^{-1}\) region exhibit shifted to lower than free xepamet (1622.13; 1587.42; 1078.28; 686.66 cm\(^{-1}\)). In the two band 1604.77 and 1585.49 cm\(^{-1}\) attributed to C=N stretching while in the band 1053.58 and 607.58 cm\(^{-1}\) attributed to C-S stretching. The bands shift to the lower frequency than free xepamet indicates that the functional group of C=N and C-S are coordinated to the metal ion Cu\(^{2+}\). New bands appeared in the low-frequency region for Cu-N at 459.06 cm\(^{-1}\) and Cu-S at 607.58 cm\(^{-1}\) which give good evidence of Cu-N and Cu-S bonds in the studied complex as in $\text{[Cu(L\textsubscript{2})](ClO\textsubscript{4})\textsubscript{2}}$, $\text{L}^2=2-(1,3$-\textit{benzothiazole}-2-yl-methyl)-1,3-\textit{benzothia-zole}$ Cu-N at 450 cm\(^{-1}\) and Cu-S at 610 cm\(^{-1}\) [10]. IR absorption bands other complexes which are similar to $\text{[Cu(xepamet)\textsubscript{2}]SO\textsubscript{4}.4H\textsubscript{2}O}$ complex are shown in table 4.
Table 4. IR absorption bands other complexes which is similar to [Cu(xepamet)₂]SO₄.4H₂O complex

| No. | Complex                                | IR absorption band of          |
|-----|----------------------------------------|--------------------------------|
| 1.  | [Cu(bemims)₂]X₂, bemims = bis[(2-ethyl-5-methyl-imidazo-4-yl)methyl]sulfide | (C=N) in 1637 and 1544 cm⁻¹, (C-S) in 1032 cm⁻¹ indicates coordination of nitrogen atom imidazol and sulfur atom to Cu²⁺ ion [11]. |
| 2.  | [Cu(DIPO)Cl₂], DIPO = 1,3-di(1H-imidazol-1-yl)-2-propanol | (C=N) in 1521 cm⁻¹ (sh) and 1506 cm⁻¹, (C-S) in 1032 cm⁻¹ indicates coordination of nitrogen atom imidazol to Cu²⁺ ion [12]. |
| 3.  | [CuL][ClO₄]₂, L=2-(1,3-benzothiazole-2-yl-methyl)-1,3-benzothiazol | (C=N) in 1621 cm⁻¹, (Cu-N) in 450 cm⁻¹ and Cu-S in and in 610 cm⁻¹ [10]. |

3.7. Magnetic properties

Magnetic susceptibility measurements of the solid complex gave magnetic moments of 1.78, B.M., showing that S = ½ for Cu(II). This value indicates that the complex is mononuclear and lack of Cu-Cu bond. This value is similar to other complex such as [Cu(L₃)₂], L₃ = 2-(4-nitrophenylaminocarbonyl) benzoic acid which has magnetic moments of 1.79 BM and the complex is a square planar structure [13].

3.8. Electronic spectra

The electronic spectra of the complex recorded in water and the observed values are shown in Table 5. The electronic spectra of the complex [Cu(xepamet)₂]SO₄.4H₂O shows one broad peak at λₘₐₓ 608 nm (16447.39 cm⁻¹). The absorption band shows d-d transition of ³B₁g → ¹A₁g as in [Cu(L₂)₂], L₂ = 1-(2-hydroxyphenyl)-3-phenyl-2-propen-1-one,N₂-(3,5-dimethyl-1H-pyrazol-1-yl)methyl]-hydrazone at 16120 cm⁻¹ [14] and in [Cu(L₅)]Cl₂, L₅ = (2E,3E)-N₁,N₂-bis(1-(2-oxo-2H-chromen-3-yl)ethylidene)ethane-1,2-diamine at 16120-16570 cm⁻¹ which both complexes indicate square planar geometry [15].
3.9. Complex Structure

The suggested structure of $[\text{Cu}(\text{xepamet})_2]\text{SO}_4\cdot4\text{H}_2\text{O}$ complex is a square planar geometry with (C=N) imidazole and (C-S) coordinated to copper(II) ion as shown in figure 8. According to IUPAC nomenclature, the suggested complex is named by bis-(2-cyano-1-methyl-3-\{(5-methylimidazol-4-yl)methyl\}thio)ethylguanidine copper(II) sulfate tetrahydrate.

![Complex Structure Diagram](image)

**Figure 8.** Suggested structure of $[\text{Cu}(\text{xepamet})_2]\text{SO}_4\cdot4\text{H}_2\text{O}$ complex

4. Conclusion

Complex $[\text{Cu}(\text{xepamet})_2]\text{SO}_4\cdot4\text{H}_2\text{O}$ can be synthesized by refluxing solution of copper(II) sulfatepentahydrate and xepamet in methanol for one hour. The complex is paramagnetic, probably a square planar structure with the functional group of C=N and C-S are coordinated to the metal ion Cu$^{2+}$.

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