



COMPLEXATION OF 5,5,7,12,12,14-HEXAMETHYL-1,4,8,11-TETRAAZACYCLOTETRADECA-7,14-DIENIUM DIPERCHLORATE WITH COPPER(II) ACETATE MONOHYDRATE IN IONIC LIQUID

(Pengkompleksan 5,5,7,12,12,14-Heksametil-1,4,8,11-Tetraazasiklo tetraazadeka-7,14-Dienium Diperklorat dengan Kuprum(II) Asetat Monohidrat dalam Cecair Ionik)

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Abstract

In the previous study, 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium diperchlorate, $[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ formed complex of $\text{C}_{16}\text{H}_{34}\text{N}_4\text{OCu}(\text{ClO}_4)_2$ and $\text{C}_{16}\text{H}_{32}\text{N}_4\text{Cu}(\text{ClO}_4)_2$ when reacted with copper(II) acetate monohydrate in acetonitrile and aqueous solutions, respectively. However, when the same reaction carried out in 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid, $[\text{Bmim}][\text{PF}_6]$, disproportionation took place to give bis(ethylenediamine) bis(perchlorato-O) copper(II) complex, $\text{C}_4\text{H}_{16}\text{N}_4\text{Cu}(\text{ClO}_4)_2$. X-ray study showed that the central copper atom was coordinated to two ethylenediamine ligands and two oxygen atoms of perchlorate ions in a distorted octahedral environment. Thermogravimetric Analysis (TGA) study showed the complex decomposition in one spontaneous mass loss at 260 °C due to the explosive nature of the perchlorate.

Keywords: ionic liquid, disproportionation, copper(II) complex

Abstrak

Dalam kajian yang lepas, 5,5,7,12,12,14-heksametil-1,4,8,11-tetraazasiklotetradeka-7,14-dienium diperklorat, $[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ membentuk kompleks $\text{C}_{16}\text{H}_{32}\text{N}_4\text{OCu}(\text{ClO}_4)_2$ dan $\text{C}_{16}\text{H}_{32}\text{N}_4\text{Cu}(\text{ClO}_4)_2$ apabila masing-masing bertindak balas dengan kuprum(II) asetat monohidrat dalam larutan asetonitril dan akues. Walaubagaimanapun, apabila tindak balas yang sama dilakukan dalam cecair ionik 1-butyl-3-metilimidazolium heksafluorofosfat, $[\text{Bmim}][\text{PF}_6]$, keperkadaran tidak seimbang berlaku dan menghasilkan kompleks kuprum(II) bis(etilenadiamina) bis(perklorato-O), $\text{C}_4\text{H}_{16}\text{N}_4\text{Cu}(\text{ClO}_4)_2$. Kajian X-ray menunjukkan atom kuprum berkoordinasi dengan dua ligan etilenadiamina dan dua atom oksigen ion perklorat dalam keadaan oktahedron terherot. Analisis termogravimetri (TGA) menunjukkan kompleks terurai dengan mengalami kehilangan jisim mendadak pada 260 °C disebabkan oleh sifat perklorat yang mudah meletup.

Kata kunci: cecair ionik, keperkadaran tidak seimbang, kompleks kuprum(II)

Introduction

5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,14-dienium diperchlorate, $[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ is a special macrocyclic tetraaza because it was obtained by templation when Curtis recrystallized bis(ethylenediamine) nickel in acetone [1]. Since then, many such complexes were synthesised by templation

method. Very few reports were on the interaction or mechanism for the reaction between the ligand and metals. However, there were some studies on the stability of the complexes in basic and acidic solutions in which isomerisation or decomposition may have taken place [2-4]. The discovery of a deprotonated Curtis salt $(\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4)\text{X}_2$ where $\text{X} =$ halogen has opened up a new scope to study the reaction from both synthetic and reaction point of view [5-7]. The complexation product is influenced by the type of tetraaza ligands, metal salts, and the solvents. For example, $(\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4)\text{Br}_2$ reacted with CuBr_2 and NH_4CuCl_4 was found to give $[(\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4)\text{BrCu}]\text{Br} \cdot 2\text{H}_2\text{O}$ and $[(\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4)\text{Cu}][\text{Cl}_4\text{Cu}]$ [8-9]. In our previous work on the reaction of $[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ with copper(II) acetate monohydrate, the same complex, $[(\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4)\text{Cu}](\text{ClO}_4)_2$ reported by Curtis was obtained [10].

Ionic liquid is a molten salt composed of ions and exist as liquid at ambient temperature. Its non-volatility, low vapor pressure and broad range of anion combination render them as well-known green solvent for many reactions and as an attractive alternative to conventional organic solvents [11]. Besides an ability to provide easy reaction medium, it may also involve in the reaction. The first report of synthesis in coordination chemistry using an ionic liquid was reported by Zhang et al. in 2013 where the reaction was carried out by using templation method [12]. To look at the role that ionic liquids can play in the complexation of tetraaza macrocyclic ligand with copper(II) acetate monohydrate, we decided to use $[\text{Bmim}][\text{PF}_6]$ as solvent for the reaction without using templation method. It was anticipated that the basic nature of ionic liquid will have an influence at least on the stability of the complex.

Materials and Methods

Chemicals

Ammonium perchlorate, ethylenediamine, copper(II) acetate monohydrate, 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid, $[\text{Bmim}][\text{PF}_6]$, methanol and acetone were purchased from Sigma-Aldrich and Friedemann Schmidt. All chemicals were of the analytical reagent grade (AR) and used without purification.

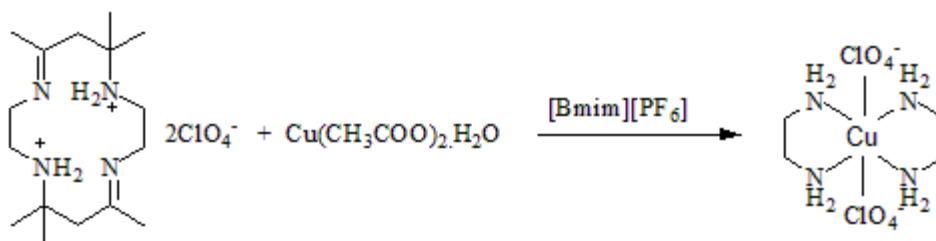
Physical measurement

Melting point was measured by using Barnstead Electrothermal Melting Point IA9100 series. Microelemental analyses were conducted using Thermo-Finnigan Flash EA 1112 Elemental Analyser. The metal content of the copper(II) complex was determined by atomic absorption technique using Perkin-Elmer AAnalyst 800 AA spectrometer. IR spectrum was recorded using FTIR Perkin-Elmer GX model with compound dispersed in KBr disks with the spectral range of $4000\text{--}400\text{cm}^{-1}$. The electronic spectrum of the complex in water was recorded on Shimadzu UV-2450 and mass spectrometry was carried out using Bruker MicroTof Q Mass Spectrometer. Magnetic susceptibility was measured using Sherwood Magnetic Susceptibility Balance (Auto) at room temperature. Thermogram was obtained by using a Mettler Toledo TGA/SDTA 851 instrument under N_2 atmosphere with a flow rate of 20 mL min^{-1} , in the temperature range of 27 to $600\text{ }^\circ\text{C}$ at the heating rate of $10\text{ }^\circ\text{C min}^{-1}$.

A single-crystal X-ray diffraction investigation was performed on Bruker D8 QUEST fitted with CCD area detectors (graphite monochromator, $\text{Mo K}\alpha$ radiation). Cell constant and an orientation matrix for data collection was obtained by least-squares refinement of diffraction data from 8144 unique reflections. The structure was solved by direct methods and refined by full-matrix least-squares techniques on F^2 using the solution program SHELXS-97 and refined using SHELXL-97 [13, 14]. Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included from the difference Fourier maps and refined with isotropic thermal parameters. Molecular drawing was obtained using MERCURY software.

Syntheses

$[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ was prepared by the same method described in the previous paper [7]. A solution of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.1 g, 0.0005 mol) in $[\text{Bmim}][\text{PF}_6]$ (5 mL) and $[\text{Me}_6\text{C}_{10}\text{H}_{16}\text{N}_4](\text{ClO}_4)_2$ (0.24 g, 0.0005 mol) in $[\text{Bmim}][\text{PF}_6]$ (5 mL) were mixed in round bottom flask. The mixture was then refluxed for 3 hours under constant stirring at $70\text{ }^\circ\text{C}$. The solution was filtered using 150 mm filter paper and extracted with water in a separating funnel. The aqueous layer was left to evaporate at room temperature. Purple crystals were obtained after one week. The crystals were washed with cold methanol, dried, and kept in a desiccator. The synthetic route of copper(II) complex is shown in Scheme 1.



Scheme 1. Synthetic route of copper(II) complex

Results and Discussion

Physical and microelemental analysis (C, H, N)

The complex was synthesised in the form of a purple solid in 79% yield. The microelemental analysis data showed an agreement with the formula of $C_4H_{16}N_4Cu(ClO_4)_2$ which was different from previous reported [7]. The yield, melting point, colour, and microelemental analysis data are shown in Table 1.

Table 1. Analytical data and physical properties of copper(II) complex

Compound	Colour	Yield (%)	Melting Point (°C)	Elemental Analysis			
				C	H	N	Cu
$C_4H_{16}N_4Cu(ClO_4)_2$	Purple	79	268.5-268.9	14.16	4.41	14.92	16.23
				12.55	4.21	14.64	16.62

*Bold value = Theoretical value

Infrared spectroscopy

IR spectrum of the complex exhibited stretching frequency for NH_2 , C-H, and C-N of 3308 , 3217 cm^{-1} , 2965 cm^{-1} , and 1088 cm^{-1} , respectively as shown in Figure 1. The absence of a band at 1670 cm^{-1} which corresponded to the $\nu(C=N)$ stretch indicated the breaking of macrocyclic ring. The stretching bands at 627 cm^{-1} and 524 cm^{-1} were assigned for O-Cl-O bond of perchlorate and Cu-O bond, respectively [15,16]. The band at 476 cm^{-1} was assigned for $\nu(Cu-N)$ according to Nakamoto and Carthy [17].

Table 2. IR spectral data of Curtis ligand and copper(II) complex

Compound	$\nu(NH_2)$	FTIR wavenumbers (cm^{-1})						
		$\nu(N-H)$	$\nu(C-H)$	$\nu(C=N)$	$\nu(C-N)$	$\nu(Cl-O)$	$\nu(Cu-N)$	$\nu(Cu-O)$
$C_{16}H_{34}N_4(ClO_4)_2$ (Ligand)	-	3466-3407 (stretch)	2981	1667	1079	623	-	-
$C_4H_{16}N_4Cu(ClO_4)_2$ (Complex)	3308, 3217	1580 (bend)	2965	-	1088	627	476	524

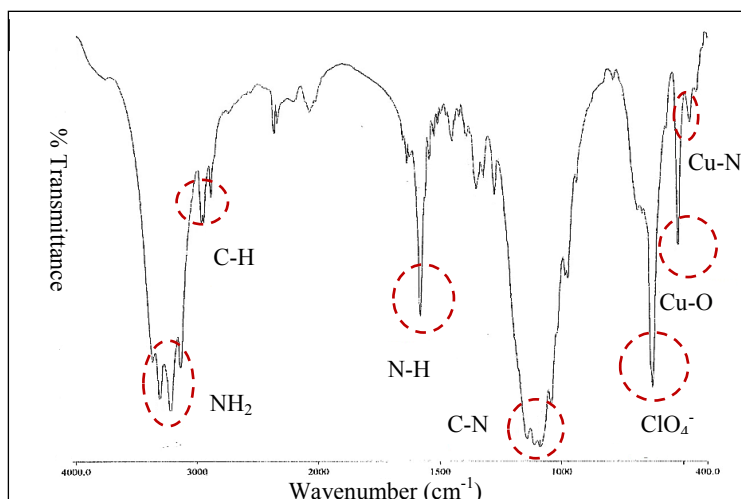


Figure 1. The FTIR spectrum of copper(II) complex

Mass spectrometry

The ESI-mass spectrum was measured to confirm the composition and purity of the complex under investigation. Representative mass spectrum of a solution containing copper(II) complex in the positive ion mode is shown in Figure 2. The ESI mass spectrum that contained molecular ion peak at m/z 381.18 was attributable to $[M-H]^+$. The molecular ion peak was in good agreement with the expected value of the copper(II) complex molecular weight. The peaks at m/z 281.24, 343.15 and 643.37 were assigned to $[M^+ - ClO_4^- - H^+]$, $[M^+ - ClO_4^- + Na^+ + K^+ - H^+]$, and $[M^+ - 2ClO_4^- - Na^+ + K^+]$, respectively. These assignments were based on ^{63}Cu .

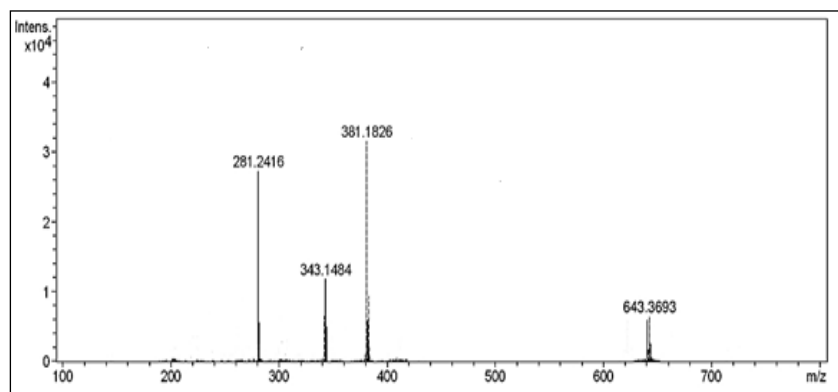


Figure 2. ESI mass spectrum in positive ion mode of copper(II) complex

Electronic spectral analysis

The UV-Vis spectrum of the complex is shown in Figure 3. The electronic spectra showed two characteristic absorption peaks at 229 nm ($\epsilon = 1370.0 \text{ Lmol}^{-1}\text{cm}^{-1}$) and 547 nm ($\epsilon = 1.7 \text{ Lmol}^{-1}\text{cm}^{-1}$) which were assigned for $\pi \rightarrow \pi^*$ and $d-d$ transition, respectively [6]. However, the maximum absorption at 547 nm was obtained at high concentration because of low extinction coefficient.

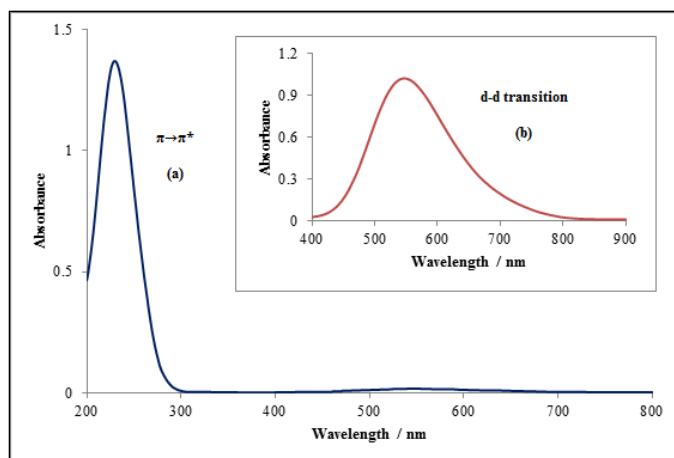


Figure 3. Absorption spectra of copper(II) complex (a) at 0.001 mol.L⁻¹ and (b) at 0.01 mol.L⁻¹

Magnetic susceptibility determination

The magnetic susceptibility measurement in the solid state showed that the present complex was paramagnetic at room temperature. The magnetic moment value ($\mu_{\text{eff.}}$) of the complex was 1.82 B.M. for paramagnetic copper with octahedral geometry and lies within the range normally found for other copper(II) complexes [18].

Thermal analysis

Thermogram of the complex (Figure 4) showed its stability up to 260 °C followed by spontaneous mass loss with residual amount of 5.46%. Such behaviour corresponded to the loss of organic moiety in the complex [7].

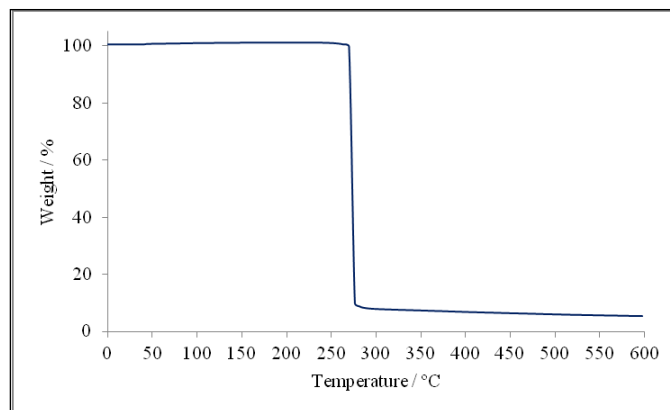


Figure 4. TGA curve of copper(II) complex

X-ray crystallography

Crystal structure of copper(II) complex, $\text{C}_4\text{H}_{16}\text{N}_4\text{Cu}(\text{ClO}_4)_2$ as shown in Figure 5 agreed with the data obtained from the physicochemical and the spectral studies. The structure of copper(II) complex was determined in a single crystal X-ray diffraction study. The X-ray of the single crystal structure for this copper(II) complex showed that the complex has a monoclinic system with a space group C 2/m, unit cell dimension with $a = 12.4825(13)$ Å, $b = 9.6470(11)$ Å and $c = 5.7256(6)$ Å; $\alpha = 90^\circ$, $\beta = 104.31^\circ$ and $\gamma = 90^\circ$. The crystallographic data, conditions for the collection of intensity data, and some features of the structure refinements are listed in Table 3. This complex formed an octahedral coordination with four nitrogen atoms in the basal plane and a definite coordination of two oxygen atoms from the perchlorate anion on the axial sites of the complex. The two Cu-O bonds (2.587 Å) were

considerably shorter than the Van der Waals radii of copper and oxygen which was 2.92 Å and therefore proved that there was a definite coordination of oxygen to the copper centre. The selected bond lengths and bond angles are shown in Tables 4 and 5.

Table 3. Details of crystallographic data collection and structure refinement parameters

State	Data
Empirical formula	C ₄ H ₁₆ Cl ₂ Cu N ₄ O ₈
Formula weight	382.65
Temperature	300(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/m
Unit cell dimensions	a = 12.4825(13) Å α = 90° b = 9.6470(11) Å β = 104.309(3)° c = 5.7256(6) Å γ = 90°
Volume	668.08(12) Å ³
Z	2
Density (calculated)	1.902 Mg/m ³
Absorption coefficient	2.075 mm ⁻¹
F(000)	390
Crystal size	0.500 x 0.170 x 0.160 mm ³
Theta range for data collection	3.369 to 28.316°.
Index ranges	-16 ≤ h ≤ 15, -12 ≤ k ≤ 12, -6 ≤ l ≤ 7
Reflections collected/unique	8144, 882 [R(int) = 0.0437]
Completeness to theta=28.32	99.8%
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	882 / 4 / 65
Goodness-of-fit on F ²	1.159
Final R indices [I > 2σ(I)]	R ₁ = 0.0384, wR ₂ = 0.0890
R indices (all data)	R ₁ = 0.0446, wR ₂ = 0.0921
Largest diff. peak and hole	0.437 and -0.555 e.Å ⁻³

Table 4. Selected bond lengths [Å] for the copper(II) complex

Bond	Bond length/[Å]
Cu(1)-N(1)	2.011(3)
Cu(1)-N(1)	2.011(3)
Cu(1)-N(1)	2.011(3)
Cu(1)-N(1)	2.011(3)
Cu(1)-O(1)	2.587(3)
Cu(1)-O(1)	2.587(3)

Table 5. Selected bond angles [°] for the copper(II) complex

Bond	Bond angle/[°]
N(1)-Cu(1)-N(1)	180.0
N(1)-Cu(1)-N(1)	95.30(18)
N(1)-Cu(1)-N(1)	84.70(18)
N(1)-Cu(1)-N(1)	84.70(18)
N(1)-Cu(1)-N(1)	95.30(18)
N(1)-Cu(1)-N(1)	180.0

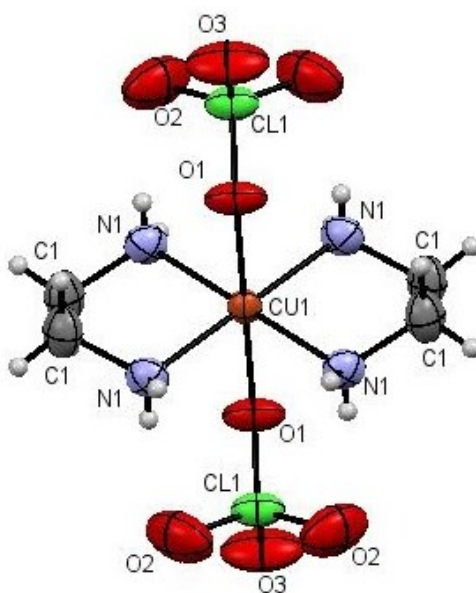


Figure 5. The ORTEP drawing of $C_4H_{16}N_4Cu(ClO_4)_2$ drawn at 50% probability ellipsoid

Conclusion

In the present communication, we have successfully synthesised and characterised copper(II) complex, $C_4H_{16}N_4Cu(ClO_4)_2$ in ionic liquid, [Bmim][PF₆]. Mass spectrum under ESI-condition was in line with the microelemental analysis, confirming the composition of the Cu(II) complex. Based on the analytical and spectral data, we assumed that the Cu(II) complex exhibited an octahedral geometry. TGA studies suggested that the complex was thermally stable up to 260 °C before the major decomposition due to the loss of the organic moiety in the complex. X-ray crystallography also showed that copper ion was bound to two ethylene diamine ligands and two oxygen atoms of perchlorate ion forming an octahedral coordination. The full mechanism of this reaction is still under investigation as we are looking at the effect of using different types of ionic liquids in this reaction. We believe ionic liquid does not act only as a solvent but is also involved in this reaction.

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