

การสังเคราะห์สารเชิงซ้อนคอปเปอร์ซีลีเนียม



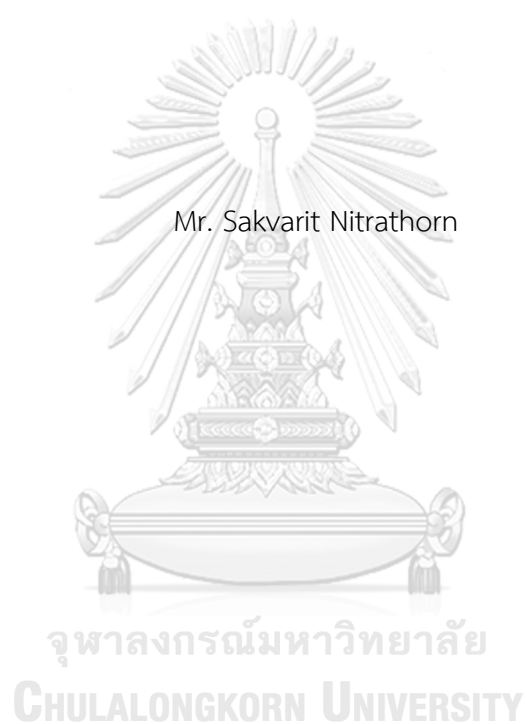
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SYNTHESIS OF COPPER-SELENIUM COMPLEX



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Chemistry

Department of Chemistry

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Thesis Title SYNTHESIS OF COPPER-SELENIUM COMPLEX
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งานวิจัยนี้มีวัตถุประสงค์เพื่อสังเคราะห์โครงข่ายอินทรีย์โลหะจากลิแกนด์ที่มีซีลีเนียม และศึกษาโครงสร้างผลึกของโครงข่ายอินทรีย์โลหะจากลิแกนด์ที่มีซีลีเนียมที่สังเคราะห์ได้ โครงข่ายอินทรีย์โลหะนั้นสามารถถูกออกแบบได้หลากหลายขึ้นอยู่กับชนิดของโลหะอะตอมกลางและลิแกนด์เชื่อมต่อ สารประกอบอินทรีย์ที่มีซีลีเนียมเป็นสารที่พบได้ค่อนข้างยาก แต่เป็นทางเลือกในทางยา ในงานนี้ได้ทำการสังเคราะห์ลิแกนด์ที่มีซีลีเนียมจากปฏิกิริยาซิฟเบสและปฏิกิริยาฟรีเดล-คราฟท์ เอซิลเลชัน แต่จากผลการทดลอง พบว่าไม่สามารถสังเคราะห์ลิแกนด์ที่มีซีลีเนียมได้จากปฏิกิริยาดังกล่าว อีกส่วนหนึ่งได้ทำการสังเคราะห์สารประกอบเชิงซ้อนจากลิแกนด์ที่มีซีลีเนียมที่มีชายในเชิงพาณิชย์ คือ ซีลีไนต์ไอออนจากโซเดียมซีลีไนต์และซีลีโน-แอล-ซิสทีนซึ่งเป็นกรดอะมิโน จากการทดลองการสังเคราะห์สารประกอบเชิงซ้อนด้วยลิแกนด์ซีลีไนต์ไอออนกับคอปเปอร์อะซิเตต โดยเพิ่ม 4,4'-ไบไพริดีนเป็นลิแกนด์ร่วม ด้วยวิธีไฮโดรเทอร์มัล พบว่าที่อุณหภูมิ 170 องศาเซลเซียสผลิตภัณฑ์ที่ได้มีลักษณะเป็นรูปเหลี่ยมสีน้ำเงินเข้ม ผลึกที่ได้สามารถนำไปหาโครงสร้างได้ด้วยเทคนิคการกระเจิงแสงของผลึกเดี่ยว พบว่ามีหน่วยเซลล์เป็นลูกบาศก์ มีกลุ่มช่องว่างเป็น $P2_13$ ในโครงสร้างนั้นพบเฉพาะโลหะทองแดงและลิแกนด์ซีลีไนต์ไอออน เกิดพันธะโคออร์ดิเนตโคเวเลนต์กันและเชื่อมต่อกันจนเกิดเป็นโครงข่ายสามมิติ เมื่อเปรียบเทียบกับงานอื่นที่ใช้ลิแกนด์ซีลีไนต์และโลหะทองแดงเหมือนกัน พบว่าโครงสร้างผลึกที่พบแตกต่างจากงานวิจัยอื่น เพราะโลหะทองแดงในงานวิจัยนี้เกิดพันธะเป็นพีระมิดฐานสี่เหลี่ยมบิดเบี้ยว ซึ่งเกิดจากการที่ใช้สารตั้งต้นเป็นคอปเปอร์อะซิเตตซึ่งมีโครงสร้างเป็นพีระมิดฐานสี่เหลี่ยม แตกต่างจากการใช้เกลือของทองแดงชนิดอื่นที่จะมีการจับกันของพันธะเป็นทรงแปดหน้า ในส่วนของการสังเคราะห์สารประกอบเชิงซ้อนจากลิแกนด์ซีลีโน-แอล-ซิสทีน หลังจากทำการผสมกันที่อุณหภูมิห้อง พบว่าสารที่ได้เป็นของแข็งลักษณะคล้ายดินเหนียวสีฟ้า ไม่มีความเป็นผลึก จึงนำไปวิเคราะห์ด้วย FTIR พบว่าสัญญาณการสั่นของพันธะระหว่างทองแดงและออกซิเจนหายไปจากตำแหน่ง 685 cm^{-1} แต่เนื่องจากขีดจำกัดของเครื่องมือ จึงไม่สามารถเก็บข้อมูลสัญญาณในช่วงความถี่ที่น้อยกว่า 650 cm^{-1} ได้

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SAKVARIT NITRATHORN: SYNTHESIS OF COPPER-SELENIUM COMPLEX. ADVISOR: PROF. NONGNUJ MUANGSIN, Ph.D., CO-ADVISOR: ASST. PROF. KITTIPONG CHAINOK, Ph.D., pp.

This research proposed to synthesize metal-organic frameworks (MOFs) from selenium-containing ligands and to study crystal structures of synthesized MOFs. MOFs can be designed in many ways, depended on types of metal center and linkage ligands. Selenium-containing organic molecules were rarely found, but they were a good choice for medical field. In this work, we tried to synthesize selenium-containing ligands from Schiff base reaction and Friedel-Craft acylation. However, the reactions were unsuccessful. In the other hand, we synthesized a coordination compound from commercial ligands, selenite ion from sodium selenite and seleno-L-cystine, which is amino acid. The experiment results showed that dark blue block shape crystals were obtained from the reaction of copper(II) acetate, selenite ion, and 4,4'-bipyridine using hydrothermal method at 170 °C. The crystal was determined using single crystal X-ray diffraction technique. The unit cell of crystal was cubic with space group of $P2_13$. The structure was grown to be a three-dimensional framework. When compare to the literature, the crystal structure was different. Coppers were in distorted square-pyramidal geometry because this work used copper(II) acetate, which is in square-pyramidal geometry; however, other's work used copper salts in octahedral geometry. In the part of seleno-L-cystine complex synthesis, which was the mixing at room temperature, the blue solid that was similar to clays and no crystallinity. The product was characterized by FTIR and found that the characteristic peaks of Cu-O stretching at 685 cm^{-1} was disappeared; nevertheless, the limitation of equipment was a problem for collecting the data at lower than 650 cm^{-1} .

Department: Chemistry

Student's Signature

Field of Study: Chemistry

Advisor's Signature

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Co-Advisor's Signature

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LIST OF ABBREVIATIONS

Cu(OAc) ₂ ·H ₂ O	copper (II) acetate monohydrate
CuCl ₂	copper (II) chloride
4,4'-bipy	4,4'-bipyridine
Pz	pyrazine
Tp	terephthalic acid
Fum	fumaric acid
Ttz	terephthalic acid hydrazide
mL	milliliters
cm ⁻¹	inverse centimeters
°C	degree Celsius
FTIR	Fourier-transform infrared spectroscopy
ATR	attenuated total reflectance
NMR	nuclear magnetic resonance spectroscopy
¹ H	proton
¹³ C	carbon-13

CHAPTER I

INTRODUCTION

1.1 Introduction

Nowadays, metal-organic framework (MOF) porous materials are interesting because they can be used in many applications¹, such as catalysts², liquid and gas separations and storages³, semiconductors⁴, ion exchange⁵, luminescence⁶, magnetic materials⁷, and drug delivery system⁸. The challenge of MOF synthesis is structure controlling by ligands designing; moreover, the structure of MOF can be conducted by coordination sites of chosen transition metal center. In this work, selenium-containing ligands were used as connecting ligands between metal ions to synthesis MOFs. The crystallographic structures of MOFs were studied by x-ray diffraction for single crystal to determine the coordination bonds of selenium-containing ligands and transition metal centers.

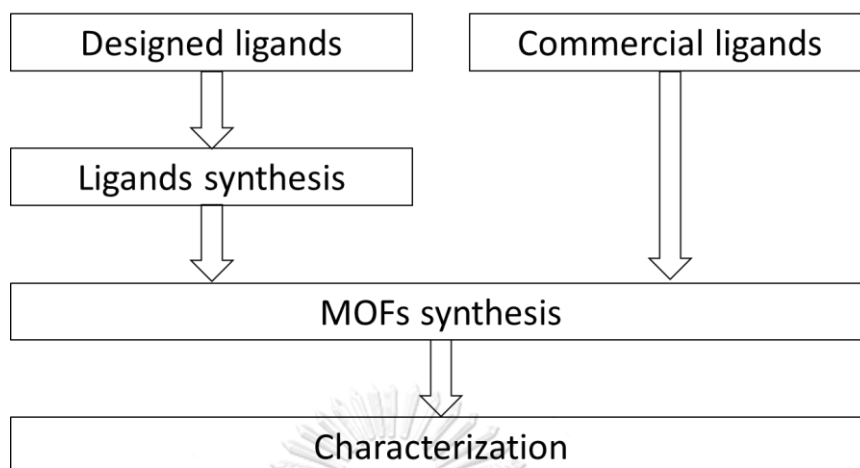
1.2 Objective

- 1.2.1 To synthesize selenium-containing molecules and use as connecting ligands
- 1.2.2 To synthesize MOFs from commercial and/or synthesized selenium-containing ligand
- 1.2.3 To determine crystal structures of synthesized MOFs

1.3 Scopes of research

- 1.3.1 Synthesize selenium containing ligands
- 1.3.2 Synthesize the coordination compound from selenium-containing ligands

1.3.3 Study the crystal structure by single crystal X-ray diffraction technique



CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Metal-organic framework (MOF)

Metal-organic frameworks (MOFs) are porous materials that consist of metal center units and organic linkers as ligands. The organic linkers are coordinated on different metal centers, and it is grown to be the open frameworks. The organic linkers which can be used for MOFs synthesis must be rigid molecule because it need to prevent the chelating effect on the same metal center. The example of suitable ligands for MOFs are shown in **Figure 2.1**.

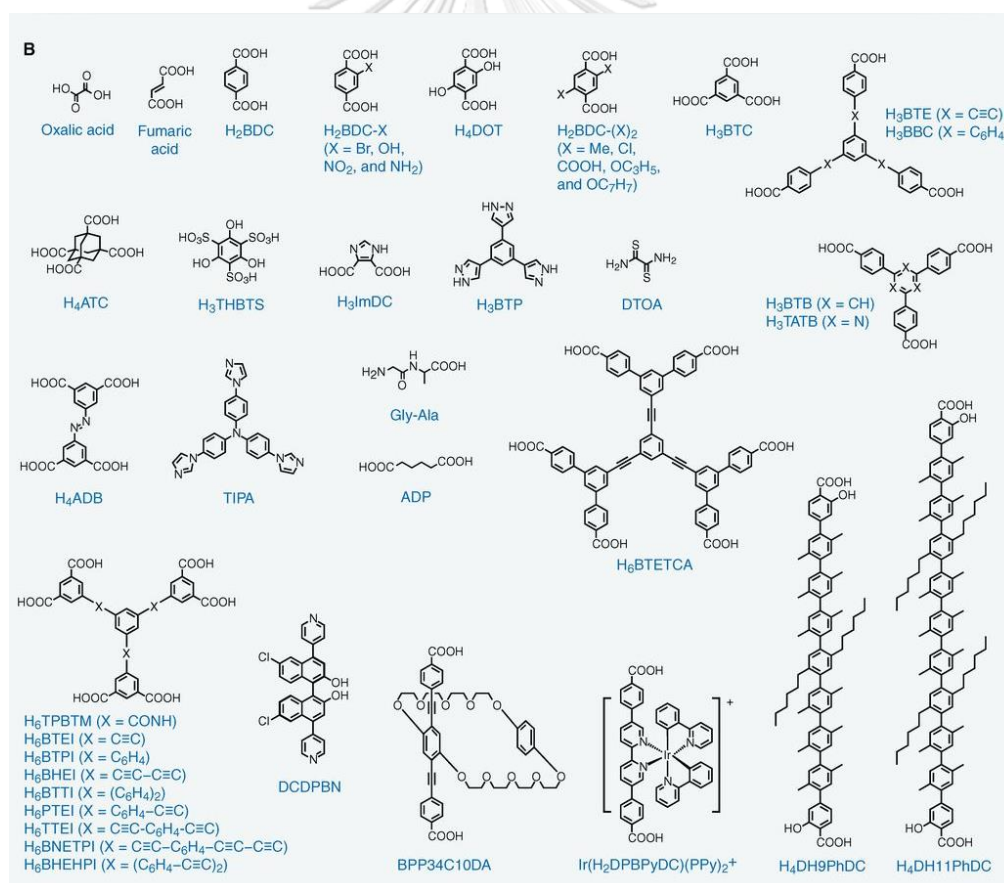


Figure 2.1 Example of organic linkers, which are used for MOFs synthesis.

When compare to other kinds of porous materials, MOFs show a lot of advantages, which are large surface areas, tunable pore size and shape, adjustable

composition, and functionalized surface. From these points, they make MOFs be suitable materials in many applications, such as catalysts, liquid and gas separations and storages, semiconductors, ion exchange, luminescence, magnetic materials, and drug delivery system.

In drug delivery system, MOFs were designed from non-toxic building blocks, and they must be biodegradable material and stable enough for using in biological experiments⁹.

In 2008, Horcajada *et al.*¹⁰ studied MOF, called MIL-53 (MIL = Material Institut Lavoisier). In this work, terephthalic acid was used as an organic linker, which linked between chromium and iron metal centers. MIL-53 was tested an ibuprofen drug encapsulation. The results showed that MIL-53 could encapsulate the ibuprofen drug longer than other materials (Figure 2.2).

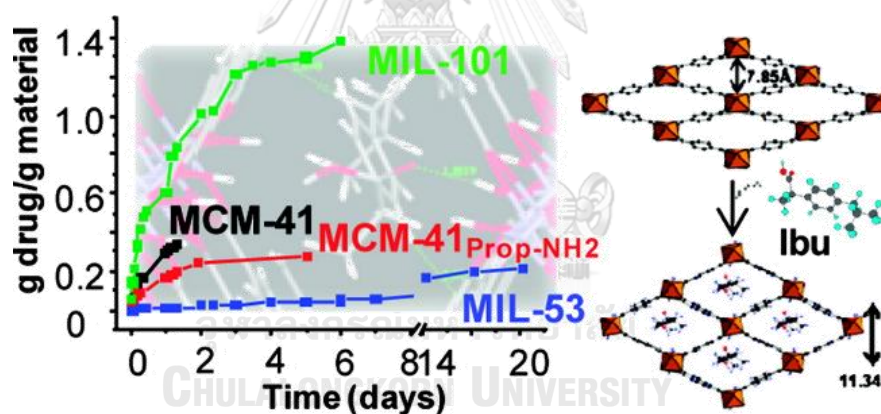


Figure 2.2 Ibuprofen encapsulation efficiency of MIL-53 compared to others and structure of MIL-53.¹⁰

In 2009, An *et al.*¹¹ synthesized Bio-MOF-1 using biphenyldicarboxylic linker and zinc-adeninate. Bio-MOF-1 was used to encapsulate procainamide drug (Figure 2.3 (A)); moreover, the drug could be released from Bio-MOF-1 by using ion exchange with sodium cation (Figure 2.3 (C)).

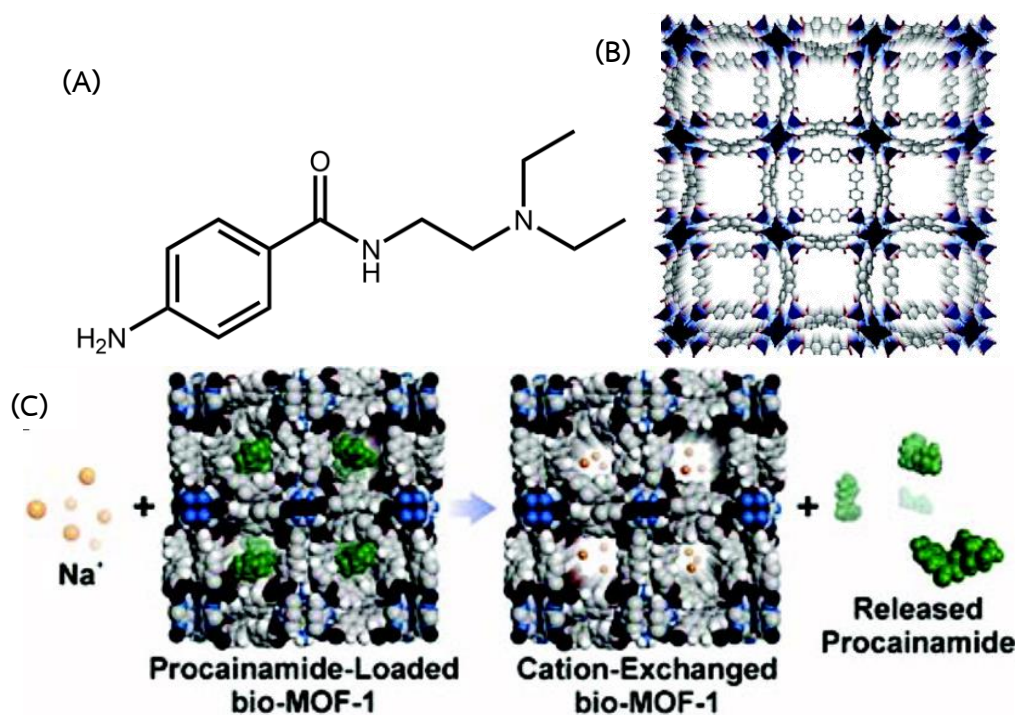


Figure 2.3 (A) procainamide chemical structure, (B) Bio-MOF-1 structure, and (C) ion exchange mechanism of procainamide drug and sodium cation¹¹

In 2014, He *et al.*¹² synthesized a nanoscale MOFs (NMOFs) for using as a cisplatin drug carrier to ovary cancer cell, called UiO. The NMOFs were synthesized from zirconium secondary building units (SBUs) and amino-triphenyldicarboxylic acid (amino-TPDC). The synthesized NMOFs were found in hexagonal plate morphologies (Figure 2.4).

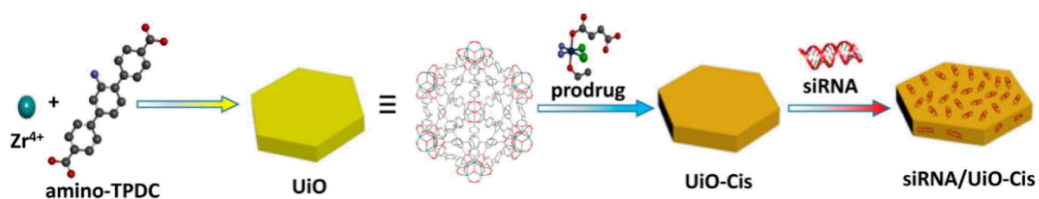


Figure 2.4 structure and cisplatin encapsulation diagram of UiO NMOFs¹²

In 2014, Hu *et al.*¹³ synthesized a low cytotoxic cationic MOF, which can change the oxidation state of iron metal center. The organic linker was 2,5-dioxido-1,4-benzenedicarboxylate. In this work, the oxidation state of iron centers was changed from +2 to +3 at 150 °C. From this phenomenon, anionic ibuprofen drug was loaded into the pores of cationic MOF (**Figure 2.5**).

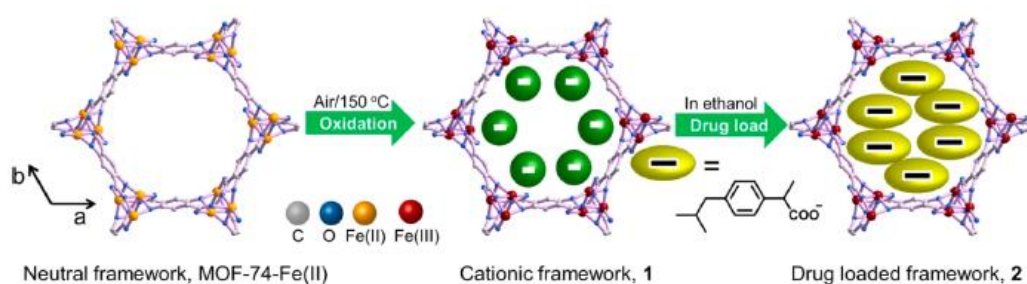


Figure 2.5 Mechanism of drug loading in cationic MOF, which can change the oxidation state of iron¹³

In 2015, Ma *et al.*¹⁴ synthesized the water-stable MOF. Zinc (II) was used as a metal center; moreover, ligands were 5-nitrosophthalate and 2,2-dimethyl-4,4'-bipyridine. This MOF was used for encapsulation and release of busulfan drug, and it could be also used in carbon dioxide separation (**Figure 2.6**).

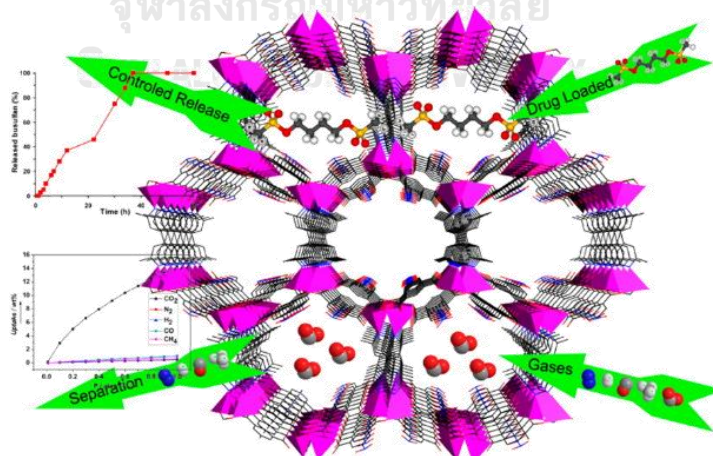


Figure 2.6 Water-stable MOF structure and its busulfan drug encapsulation and release abilities.¹⁴

2.2 Selenium-containing ligands

Selenium is an essential element for human lives. It was found in many types of selenoproteins, such as selenocysteine (SeCys), which was used for the synthesis of other types of selenoprotein¹⁵. The trace amount of selenium compounds shows various biological activities including antioxidants enzymes and using in thyroid hormones.

Selenocompounds can be used in the medical treatment, such as cancer therapy and cardiovascular disease medicine. In some works, the selenocompounds were used as ligands of coordination medicine and presented the higher activity.

In 2013, Brumaghim *et al.*¹⁶ reported the copper complex with selenium-containing ligand. In this work, selenium-containing ligand was used to prevent the oxidation of Cu^{2+} (Figure 2.7), which was necessary for DNA damage observation. From this work, they concluded that the copper coordination by selenium compounds can provide targeted sacrificial antioxidant activity.

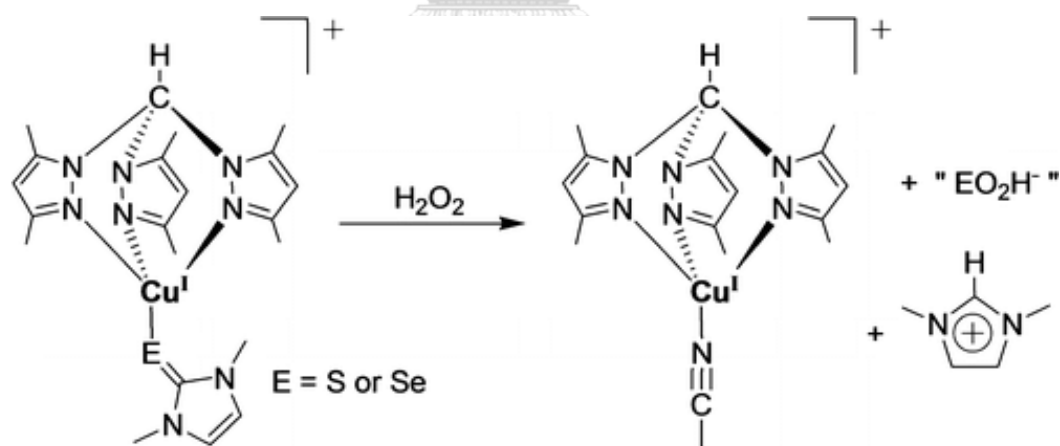


Figure 2.7 Structure of $[\text{Tpm}^*\text{Cu}(\text{L})]$ complex,

$[\text{Tpm}^* = \text{tris}(3,5\text{-dimethylpyrazolyl})\text{methane};$

$\text{L} = \text{N,N}'\text{-dimethylimidazole selone or thione}]^{16}$

In 2015, Deng *et al.*¹⁷ reported the selenium-containing ruthenium complex. The complex was used as an anticancer drug compare to cisplatin and other complex, which ligands were not selenocompounds. The results showed that the selenium-containing ruthenium complex showed better anticancer activity against A375 cancer cells (human melanoma cells) (Figure 2.8).

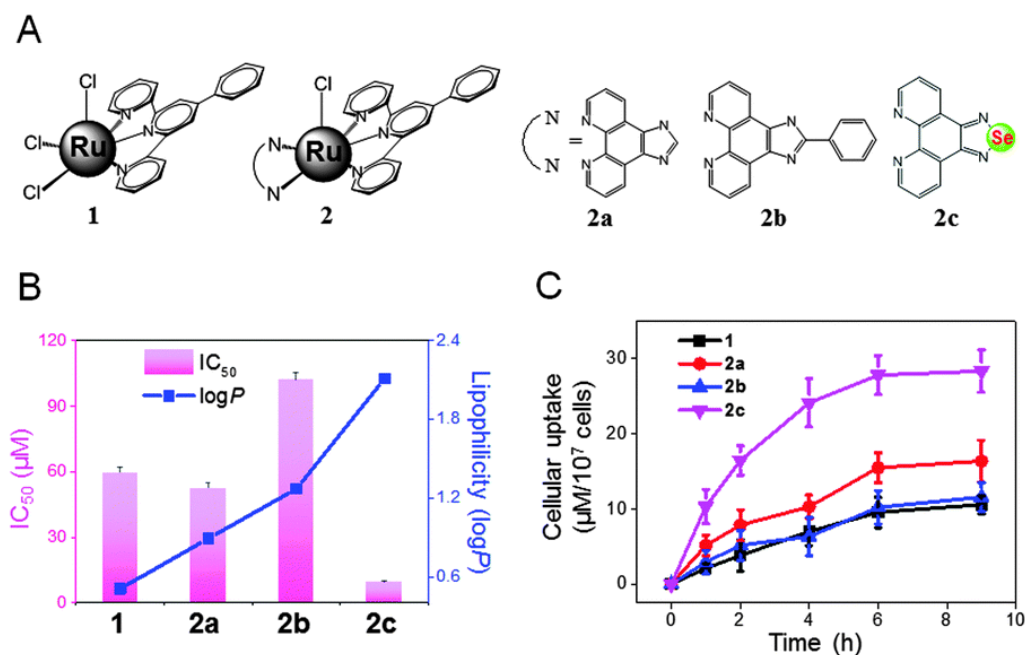


Figure 2.8 structure of ruthenium complexes and ligands, and anticancer activity against A375 cells¹⁷

In 2016, Xu *et al.*¹⁸ reported selenium-platinum coordination dendrimers, which used selenium position on dendrimers (Figure 2.9) to coordinate on cisplatin to be a drug delivery system. The results showed higher cellular uptake and anticancer activity against HepG2 liver cancer cells; moreover, the tumor volumes of mice injected with selenium-platinum coordination dendrimers were inhibited.

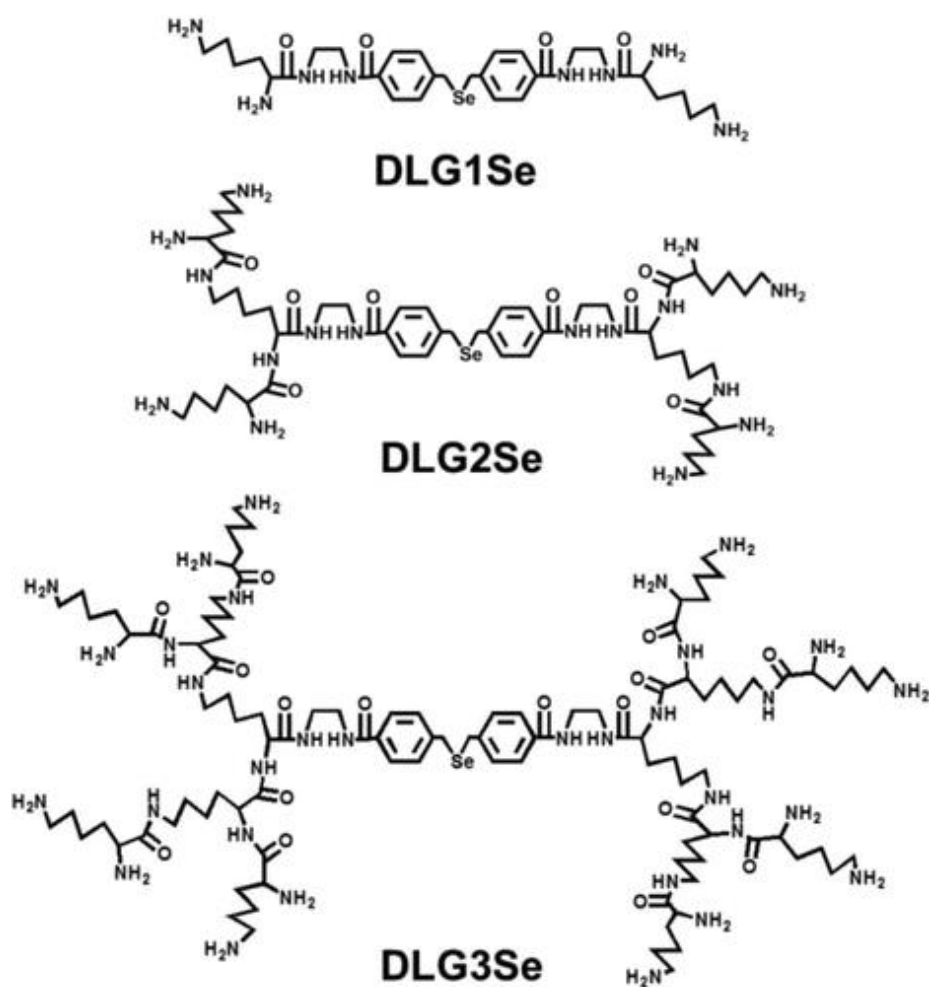


Figure 2.9 Structure of selenium dendrimers¹⁸

CHAPTER III

EXPERIMENTAL SECTION

3.1 Materials

All organic solvents were analytical reagent grade, purchased from Merck. Copper(II) acetate monohydrate and aluminium chloride anhydrous were purchased from Fluka Chemicals. Sodium selenite was purchased from Fluka Analytical. Selenourea, and seleno-L-cystine were purchased from Aldrich Chemicals. Diphenyldiselenide was purchased from Tokyo Chemical Industry. Acetyl chloride was purchased from Acros Organics. Terephthalaldehydic acid was purchased from Merck. Zinc oxide was purchased from Carlo Erba Reagents. All chemicals were used as received.

3.2 Analytical instruments

3.2.1 NMR studies

Samples were dissolved in deuterated chloroform (CDCl_3) and added into the NMR tube. ^1H -spectra were recorded using Varian Mercury NMR spectrometer operated at 400 MHz (Varian Company, CA, USA). ^{13}C -NMR was recorded using Bruker model ACF200 spectrometer operated at 400 MHz (Bruker Company). All chemical shifts were reported in ppm. The ^1H - and ^{13}C -NMR data were processed by using MestReNova software.

3.2.2 ATR FTIR studies

ATR FTIR were recorded on Nicolet FTIR impact 410 spectrophotometer. The solid samples were used as synthesized. The spectra

were recorded between 650 cm^{-1} to 4000 cm^{-1} in transmittance mode. The data were processed by OMNIC software.

3.2.3 Single crystal X-ray diffraction studies

Crystal structure determination were recorded by Bruker D8 QUEST CMOS diffractometer with $\text{Mo K}\alpha$. All diffraction data were integrated, refined, and reduced data by using Bruker *APEX3* and *SAINT* programs. *Olex2* program was used to solved and refined structure. The molecular graphic and crystallographic information file were prepared by *publCIF* program.

3.3 Selenium-containing ligands synthesis

3.3.1 Selenourea-core ligands¹⁹

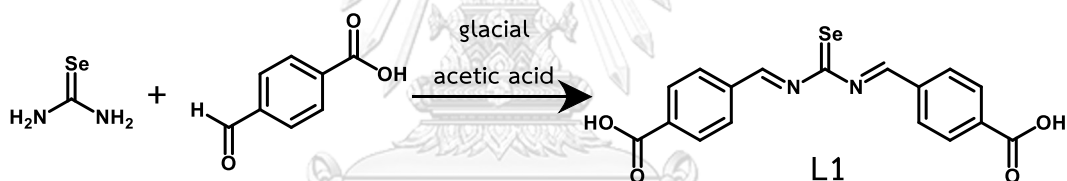


Figure 3.1 Proposed chemical reaction between selenourea and terephthalaldehydic acid (L1)

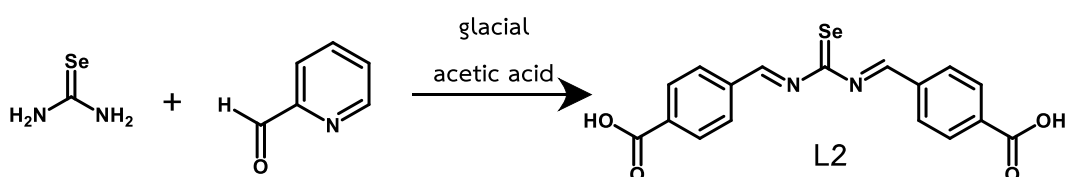


Figure 3.2 Proposed chemical reaction between selenourea and 2-pyridinecarboxaldehyde (L2)

Terephthalaldehydic acid 0.6074 g (0.4 mmol) was dissolved in 60 mL of benzene. Glacial acetic acid was dropped into the solution and stirred for

30 minutes. Then, selenourea 0.3617 g (0.2 mmol) was added and refluxed at 110 °C for 4 hours. A small amount of water was added to dissolved selenourea. After finished, the solvent was evaporated. Crude product was obtained and kept in the refrigerator. Some of product was dissolved in methanol to crystallize. Another reaction was used the same process; however, terephthalaldehydic acid was changed to 2-pyridinecarboxaldehyde (0.2935 g, 0.4 mmol). This process followed from Schiff base synthesis from urea and thiourea, which contained the same group element as selenium. (Figure 3.1, Figure 3.2)

3.3.2 Diphenyldiselenide-core ligand²⁰

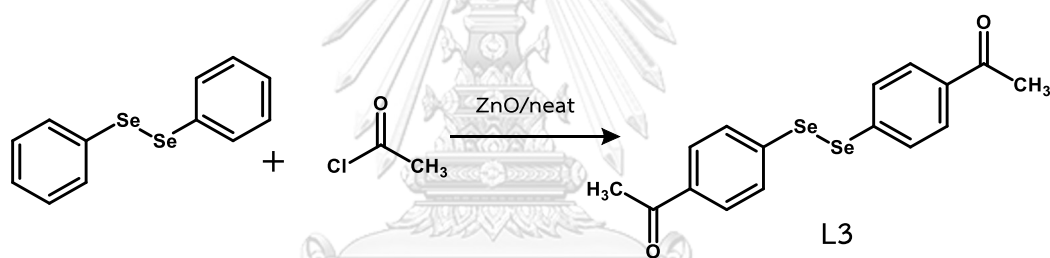


Figure 3.3 Proposed chemical reaction between diphenyldiselenide and acetyl chloride (L3)

Zinc oxide 0.0819 g (1 mmol) and acetyl chloride 0.143 mL (2 mmol) were mixed in a mortar, then diphenyldiselenide 0.3117 g (1 mmol) was added into the mortar. The chemicals were grinded for 10 minutes. After finished grinding, elute it by 20 mL of chloroform and filter zinc oxide out. The yellow solution was washed by sodium bicarbonate solution for three times, and it was dried by sodium sulfate. The solvent was evaporated and obtained the yellowish-brown liquid for characterization. The synthesis was follow to the Friedel-Craft acylation reaction (Figure 3.3).

3.4 Selenium-containing complex synthesis

3.4.1 Complex from selenite ligand²¹

A mixture of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (0.046 g, 0.25 mmol), Na_2SeO_3 (0.042 g, 0.25 mmol) and 4,4'-bipyridine (0.040 g, 0.25 mmol) in distilled H_2O (5 ml) were placed in a Teflon lined reactor, stirred at room temperature for 10 min, sealed in a 23 mL stainless steel autoclave, placed in an oven, and then heated to various temperature under autogenous pressure for 48 h. The reaction mixture was cooled to room temperature. After filtration, the product was washed with distilled H_2O and dried in air at room temperature.

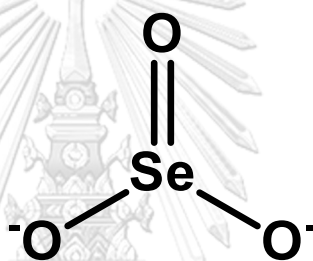


Figure 3.4 Chemical structure of selenite ligand (L4)

3.4.2 Complex from seleno-L-cystine ligand

Copper(II) acetate monohydrate 0.0199 g (0.1 mmol) was dissolved in various solvents, then seleno-L-cystine 0.0347 g (0.1 mmol) was added into the copper solution. The reactions were stirred for 30 minutes to 1 hour. The products were obtained.

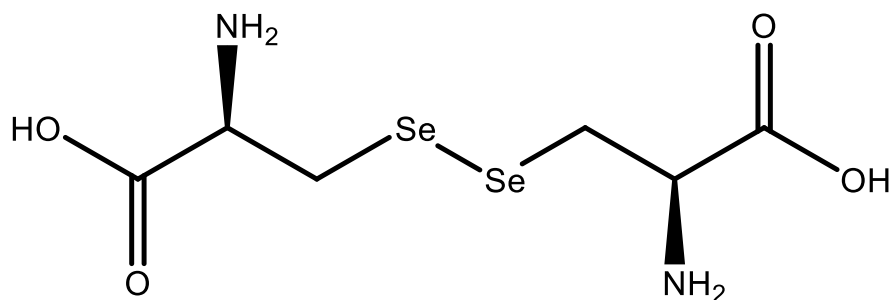


Figure 3.5 Chemical structure of seleno-L-cystine ligand (L5)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Selenium-containing ligands synthesis

4.1.1 Selenourea-core ligands (L1, L2)

The Schiff base reaction needed to eliminate the water out of the reaction, so Dean Stark apparatus was used for water trapping. After reflux and solvent evaporation, crude products were obtained from both L1 and L2 reactions. The crude products of L1 and L2 were dissolved in small amount of methanol for a recrystallization, and they were kept in a refrigerator. The obtained brown crystals of L1 and L2 were determined by single crystal X-ray diffraction; however, the unit cell determination of L1 and L2 crystals showed that the obtained crystals were terephthalaldehydic acid and 2-pyridinecarboxaldehyde from L1 and L2 synthesis, respectively. In this case, because of selenium was a large size element compared to oxygen and sulfur. Steric effect could be occurred, which made nitrogen position on selenourea were hardly reacted with the aldehyde site to form Schiff base, and lone pair electrons on nitrogen could not be donated to aldehyde site easily.

4.1.2 Diphenyldiselenide-core ligand (L3)

The product was obtained in dark yellow liquid and changed to yellow crystal after kept in the refrigerator. The yellow crystals (**Figure 4.1**) were dissolved by CDCl_3 and characterized by ^1H - and ^{13}C -NMR spectroscopy techniques. The ^1H -NMR spectrum of product was compared to spectrum of diphenyldiselenide (**Figure 4.2**). The spectra showed a peak shift from 1.65 ppm to 1.57 ppm, which was the area of C-H proton, so it was possible to be methyl groups from acetyl chloride that connected to diphenyldiselenide. To confirm this point, ^{13}C -NMR spectrum was studied. However, the spectrum showed only peaks of phenyl ring at 127, 129, and 131 ppm which was at the same position of diphenyldiselenide spectrum (**Figure 4.3**). The yellow crystal was also characterized by single crystal x-ray diffraction technique. The results showed the structure of diphenyldiselenide, which meant the Friedel-Craft acylation of diphenyldiselenide was not occurred.

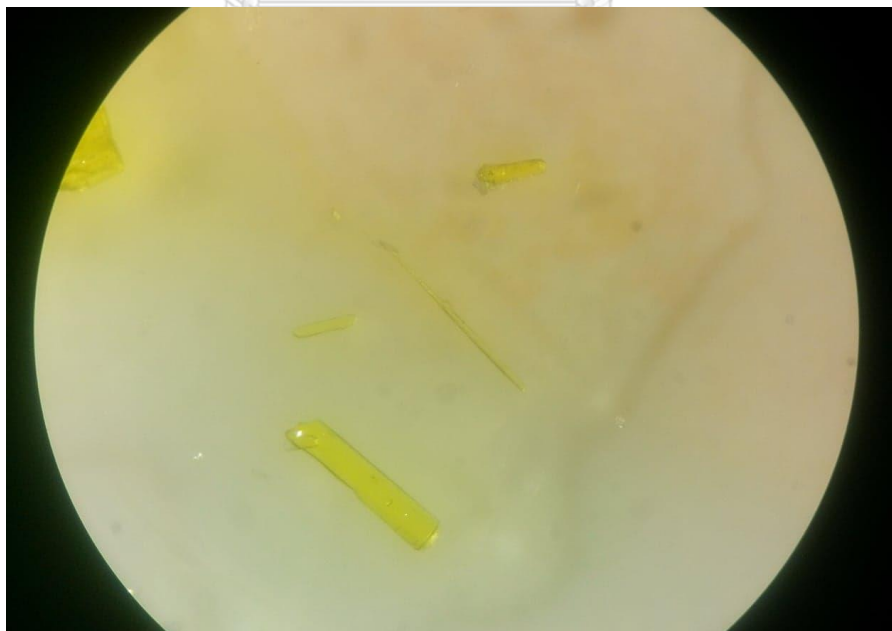


Figure 4.1 Yellow crystal of L3, observed by optical microscope

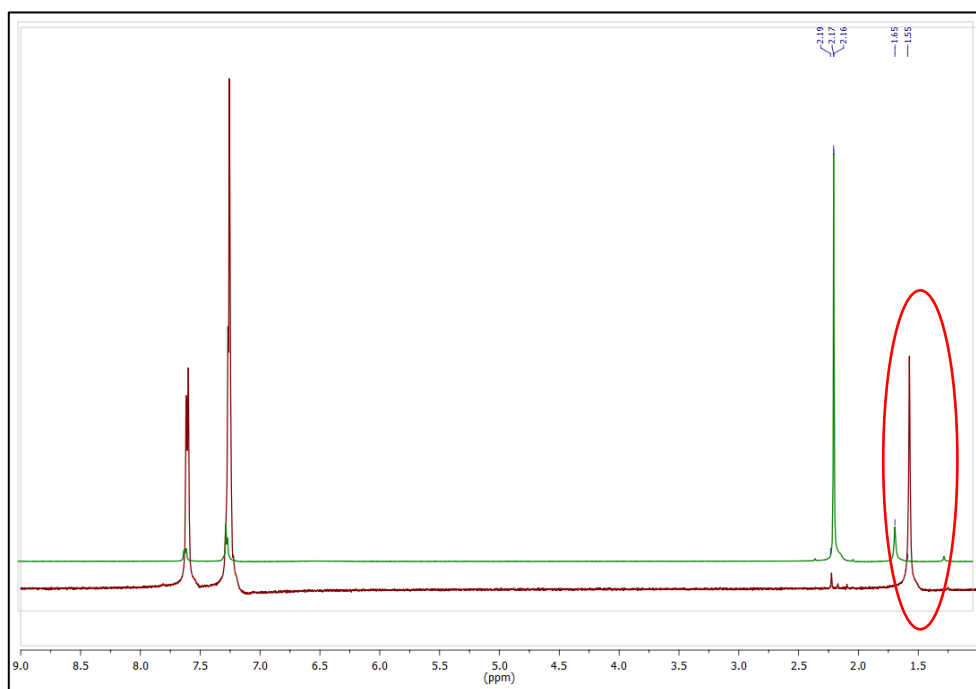


Figure 4.2 $^1\text{H-NMR}$ spectra of diphenyldiselenide (green) and synthesized product (dark red) (L3)

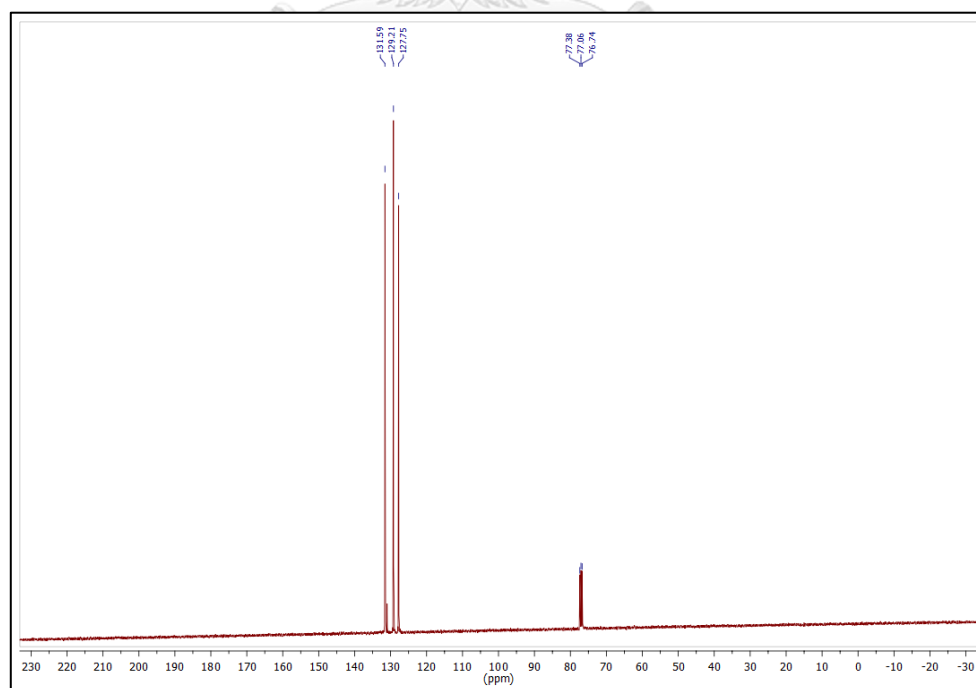


Figure 4.3 $^{13}\text{C-NMR}$ spectrum of synthesized product (diphenyldiselenide)

From these results, we found that selenium-containing organic molecules were difficult to synthesized. They cannot be synthesized by normal organic synthesis processes; however, it might be needed some special condition to synthesize. We have discussed to the reason of unsuccessfully synthesized and concluded that selenium is a large atom species, it might show the steric hindrance to an environment atom; moreover, the seleno-organic compounds are highly stable, the reaction cannot occur easily. Therefore, this research were unsuccessfully synthesized selenium-containing ligands ourselves; moreover, L1, L2, and L3 were not used for copper complexes synthesis.

4.2 Selenium-containing complex synthesis

4.2.1 Complex from selenite ligand (L4)

The syntheses were studied from various metal salts, co-ligands, and reaction temperature. From **Table 1** and **Table 2**, the results showed that good quality crystals were obtained from copper salt and 4,4'-bipyridine co-ligands experiments. The copper salt was changed from CuCl_2 to $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ to study some differences between CuCl_2 which has an octahedral geometry and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ which has a square-pyramid geometry.

Table 1 Hydrothermal synthesis of Na_2SeO_3 and various metal salts

Metal	Temperature	Product morphology
CuCl_2	160 °C	Crystal ²²
CdCl_2	160 °C	Powder
ZnCl_2	160 °C	Powder
$\text{Gd}(\text{NO}_3)_3$	160 °C	Powder
$\text{Pr}(\text{NO}_3)_3$	160 °C	Powder
FeCl_2	160 °C	Powder
MnCl_2	160 °C	Powder
CrCl_3	160 °C	Powder
CoCl_2O_8	160 °C	Powder
NiCl_2O_8	160 °C	Powder

Table 2 Hydrothermal synthesis of CuCl_2 , Na_2SeO_3 , and co-ligands

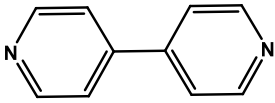
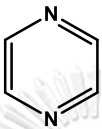
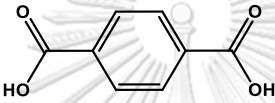
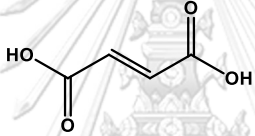
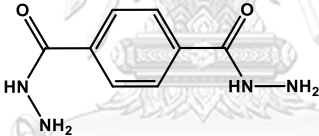
Metal	Co-ligand	Structure	Temperature	Product morphology
CuCl_2	4,4'-bipy		160 °C	Block crystal (Cu-4,4'-bipy)
CuCl_2	Pz		160 °C	Red small crystal
CuCl_2	Tp		160 °C	Small crystal
CuCl_2	Fum		160 °C	Small crystal
CuCl_2	Ttz		160 °C	Small crystal

Table 3 Hydrothermal synthesis of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, Na_2SeO_3 and 4,4'-bipy at various temperature

Metal	Co-ligand	Temperature	Product morphology
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	4,4'-bipy	170 °C	Green block crystal and yellow thin crystal
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	4,4'-bipy	150 °C	Blue spherical particles and yellow thin crystal
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	4,4'-bipy	130 °C	Blue spherical particles and yellow thin crystal
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	4,4'-bipy	110 °C	Powder
$\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$	4,4'-bipy	88 °C	Powder

Crystals were obtained from the hydrothermal synthesis. At 170 °C reaction, the green and yellow crystals were observed by optical microscope (**Figure 4.4 (A)**), which were from copper coordination compound and leftover ligand. The morphology of yellow crystals was showed in thin plate, so we did not collect these crystals for structure determination. The green crystal was collected to find its crystal structure. In addition, the experiments at lower temperature showed hexagonal yellow crystal shape, which was 4,4'-bipyridine crystals, and the blue spherical shape particles that showed in **Figure 4.4 (B)** were copper particles from 130 °C reaction, which was not form complex with ligands, and non-crystal products were obtained from the lower reaction temperature.

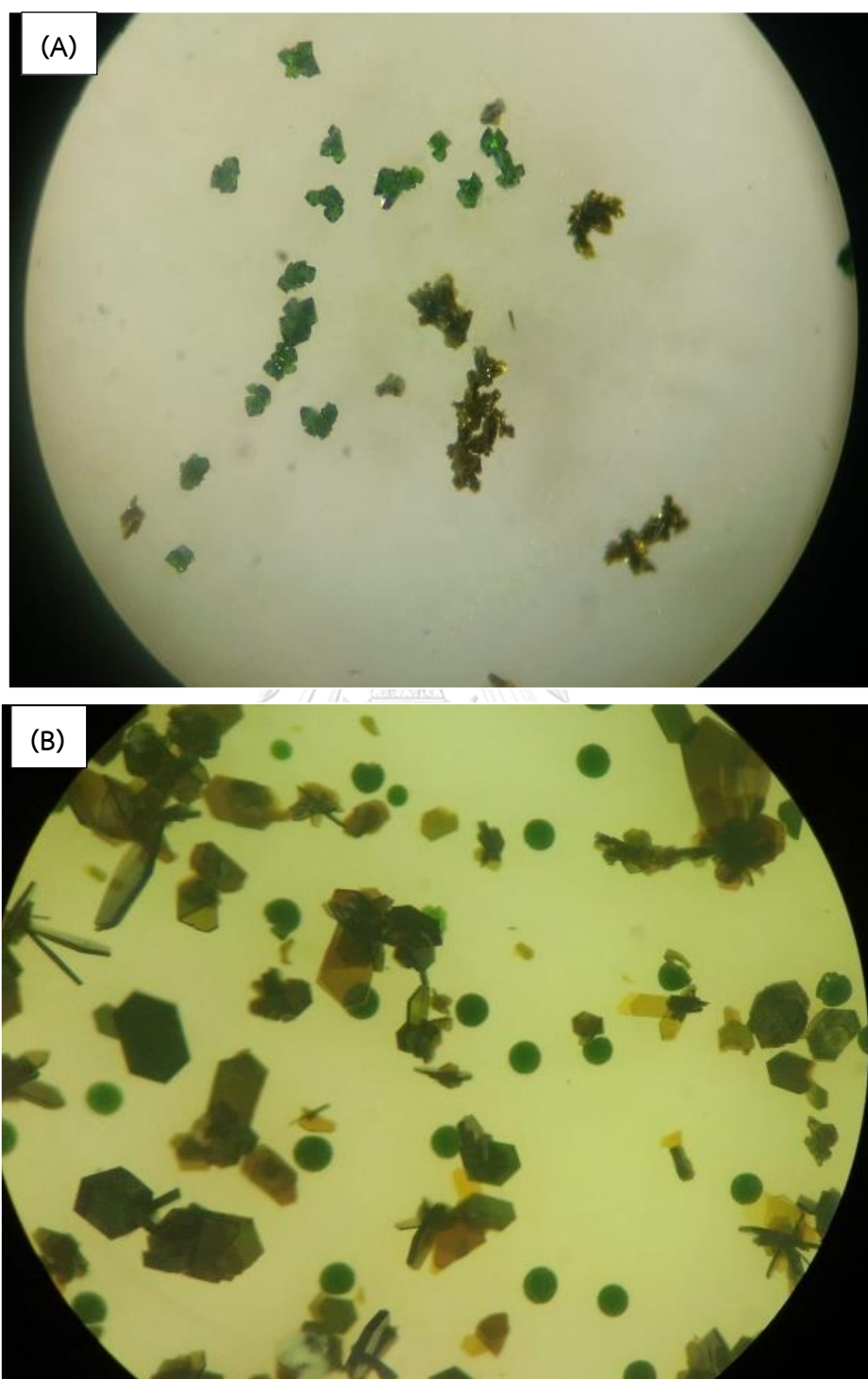


Figure 4.4 Crystals from hydrothermal method at (A) 170 °C and (B) 130 °C

Crystals were obtained from the hydrothermal synthesis. At 170 °C reaction, the green and yellow crystals were observed by optical microscope (**Figure 4.4 (A)**), which were from copper coordination compound and leftover ligand. The morphology of yellow crystals was showed in thin plate, so we did not collect these crystals for structure determination. The green crystal was collected to find its crystal structure. In addition, the experiments at lower temperature showed hexagonal yellow crystal shape, which was 4,4'-bipyridine crystals, and the blue spherical shape particles that showed in **Figure 4.4 (B)** were copper particles from 130 °C reaction, which was not form complex with ligands, and non-crystal products were obtained from the lower reaction temperature. The green crystal from 170 °C experiment was mounted in x-ray diffractometer. The crystal was observed in dark blue color and block shape. The results showed cubic crystal system and $P2_13$ space group. The structure confirmed that oxygens on selenite molecules were coordinated on copper centers with ratio of 1:1, but 4,4'-bipyridine did not coordinated, so we have confirmed that copper selenite (Cu-L4) was obtained. Oxygen atoms of selenite ligand coordinated on copper atoms. The structure was presented as coordination polymer, which showed in **Figure 4.5**. A unit of the Cu-L4 consisted of two copper atoms. There were three geometries presented on this structure, which were square pyramids of $\{CuO_5\}$, trigonal bipyramids of $\{CuO_5\}$, and trigonal pyramids of $\{SeO_3\}$ (**Figure 4.6, Figure 4.7**). The complex was growth into three-dimensional framework (**Figure 4.8**).

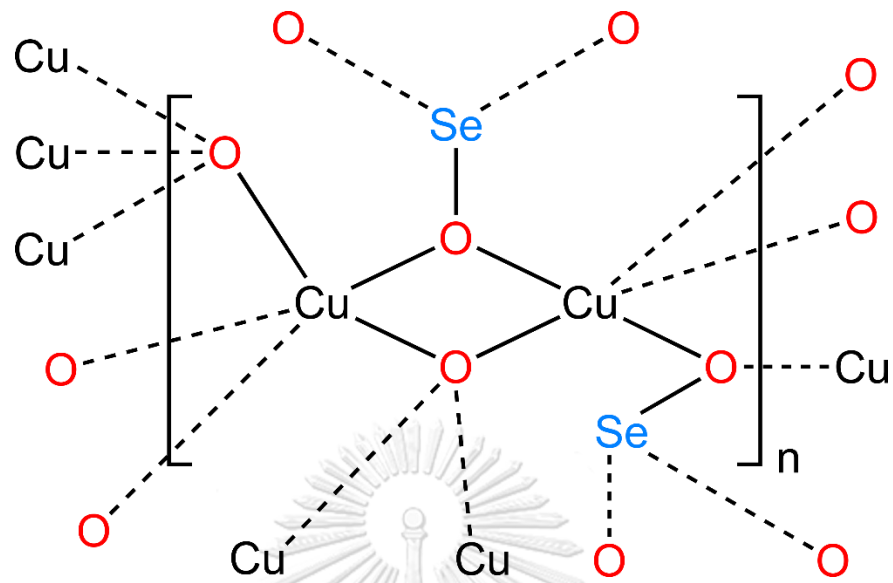


Figure 4.5 Schematic diagram of copper selenite (Cu-L4)

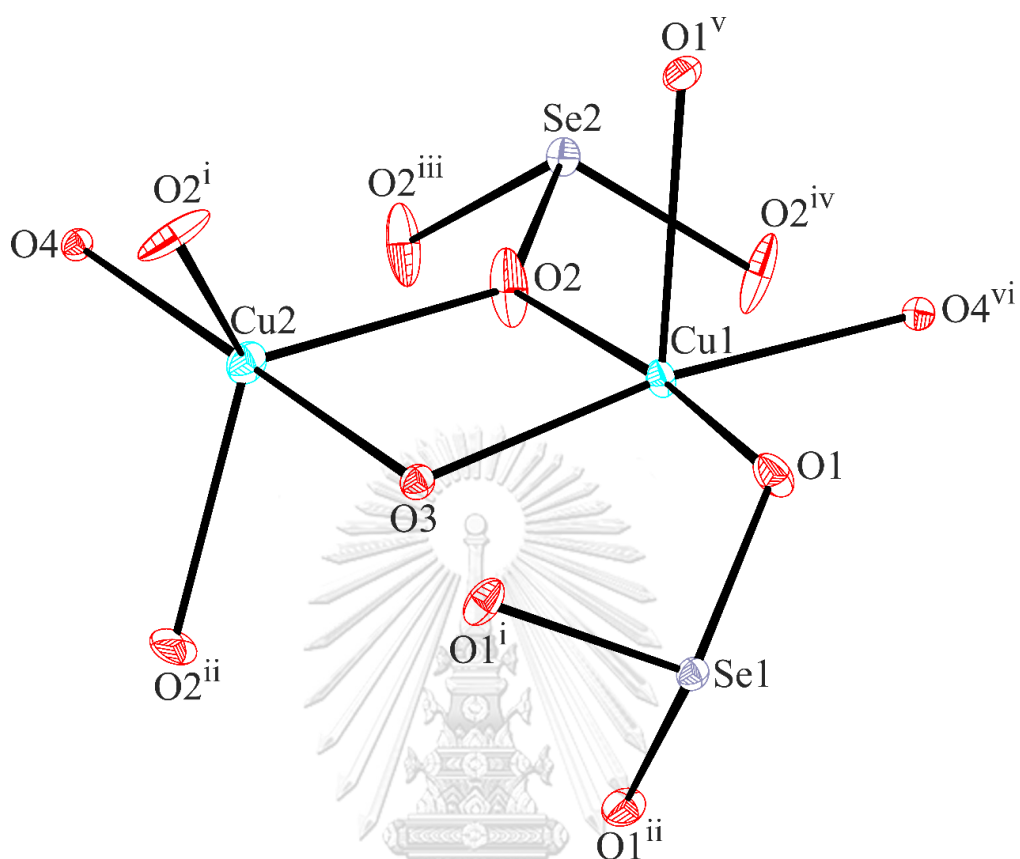


Figure 4.6 A displacement ellipsoid diagram showing the coordination around the metal centers in the title compound. Atomic displacement parameters are given at the 50% probability level. Symmetry codes: (i) $z + 1/2, -x + 3/2, -y + 1$; (ii) $-y + 3/2, -z + 1, x - 1/2$; (iii) y, z, x ; (iv) z, x, y ; (v) $-y + 1, z - 1/2, -x + 3/2$; (vi) $-x + 3/2, -y + 1, z + 1/2$.

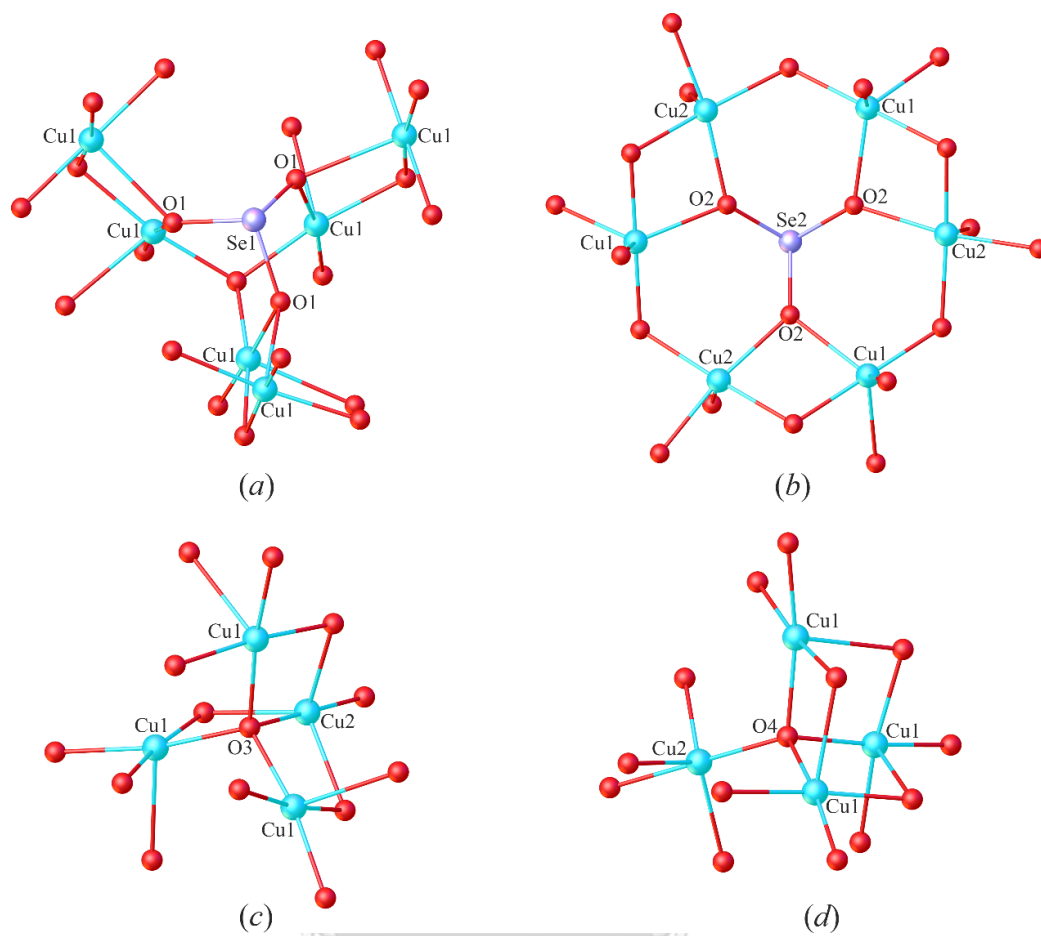


Figure 4.7 Coordination modes of the SeO_3^{2-} (a, b) and O^{2-} (c, d) anions found in the title compound.

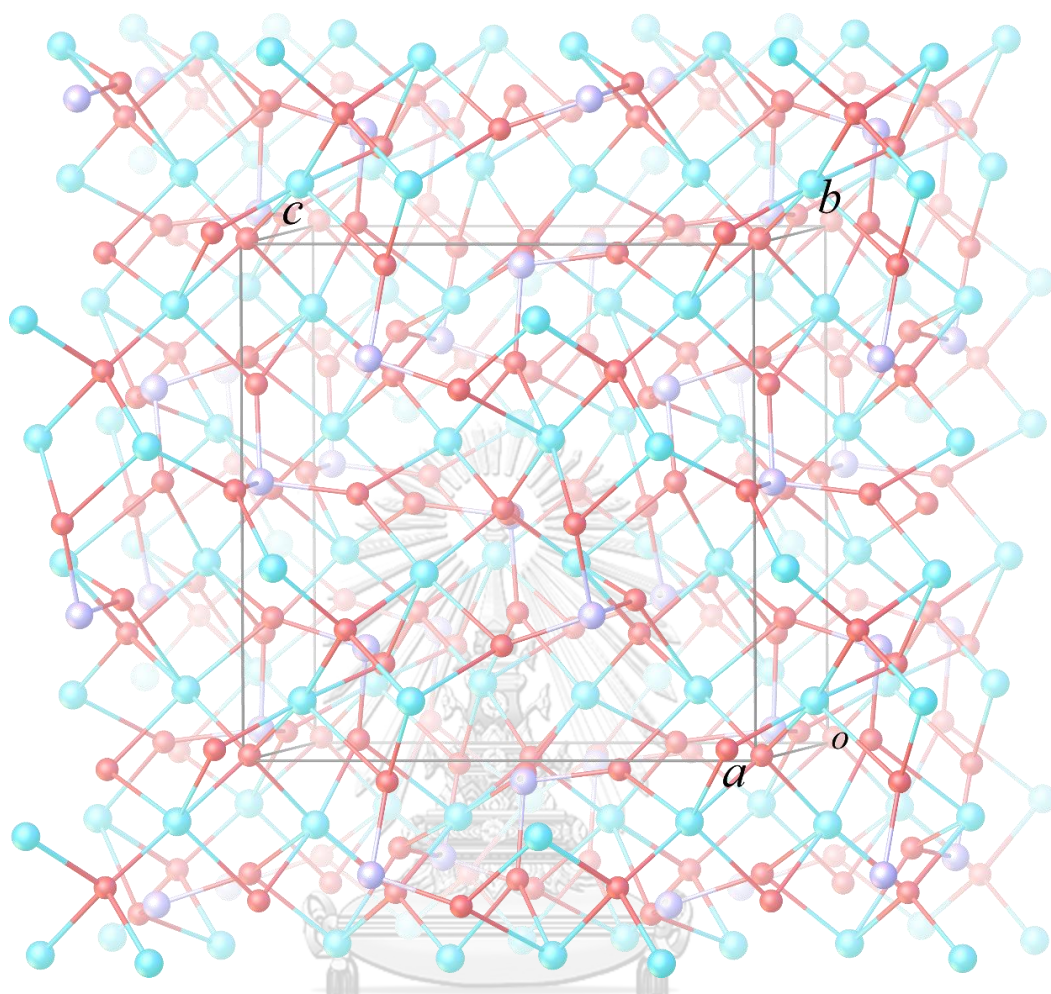


Figure 4.8 The unit cell packing in the title compound

Our structure was compared to Graiff's work²², which selenite anion was used to be a ligand to coordinate on copper centers same as our work. Their structures were crystallized in orthorhombic and monoclinic that presented space groups of $P2_12_12_1$ and $P2_1/n$, respectively. In their work, water molecules were also coordinated on copper centers, which our structure did not. The difference of their and our works were synthesis method and starting materials. Our work started with $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, which was presented in square pyramids geometry, but they started from copper(II) nitrate, which was octahedral geometry. From the position of copper centers

in our structure, it was no vacant site for the coordination of water molecules. The structure was also compared to Meunier's work.²³ The crystal structure of Cu-L4 was same as their structure; however, they synthesized copper selenite using chemical transport method at 400-450 °C. In this work, Cu-L4 was obtained from the hydrothermal method at 170 °C, which was dramatically lower than their work. Our work reported the space group of $P2_13$, but theirs were reported in two space groups, $P2_13$ or $P4_232$, which meant their data were not good enough to confirm the structure.

4.2.2 Complex from seleno-L-cystine ligand (L5)

Seleno-L-cystine was a diselenide amino acid, which was hardly to dissolved in any solvent; however, we synthesized in the water and ethanol mixed solvents. At the starting time before adding seleno-L-cystine in to the reaction, the copper(II) acetate solution was blue, but the solution was changed into colorless after seleno-L-cystine adding without dissolved and stirred at room temperature. Blue solids were obtained. The blue solids were like clays, not crystals, and it was characterized by ATR FTIR. The spectra (**Figure 4.9**) presented that Cu-O stretching at 685 cm^{-1} was disappeared; however, the equipment cannot reach lower than 650 cm^{-1} , which could not confirm those were Cu-O stretching²⁴ or not. Another important peak was Cu-N stretching around $260\text{-}270\text{ cm}^{-1}$, which were not observed because of the limitation of FTIR equipment. Therefore, we needed to find the way for crystallization and/or characterization of the product.

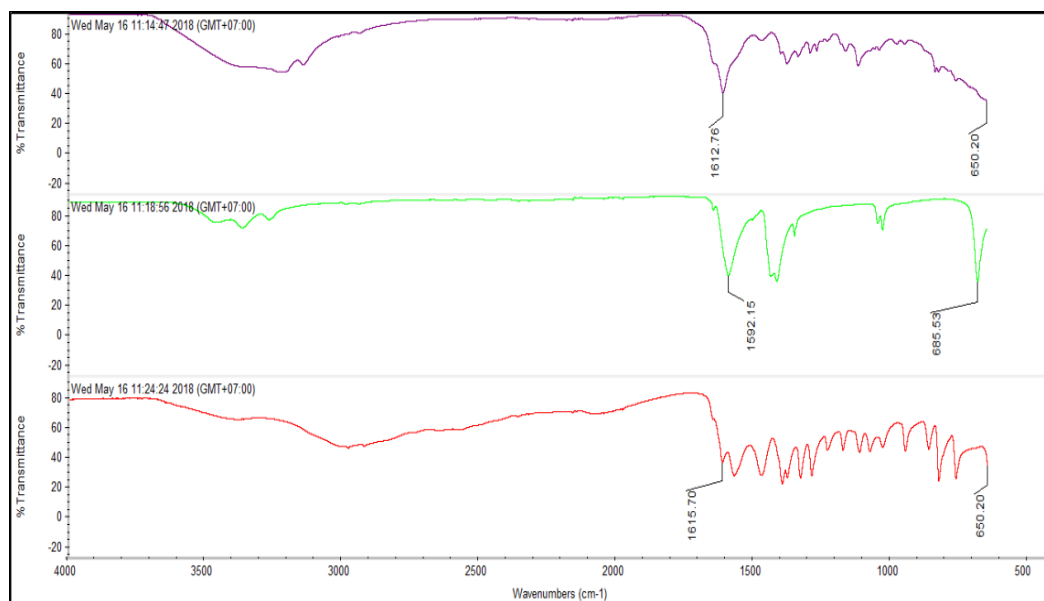


Figure 4.9 FTIR spectra of product, copper(II) acetate monohydrate, and seleno-L-cystine



CHAPTER V

CONCLUSION

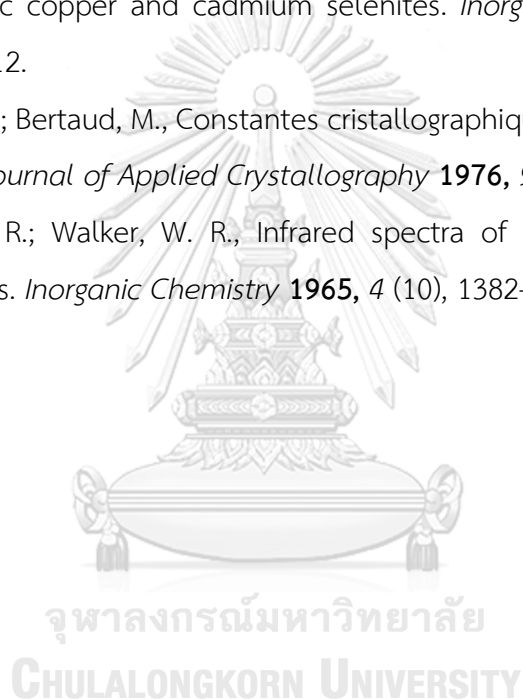
The designed selenium-containing ligands were not successfully synthesized. The unit cell determinations of L1, L2, and L3 were reported that the obtained crystals were terephthalaldehydic acid, 2-pyridinecarboxaldehyde, and diphenyldiselenide, respectively. We had successfully synthesized and crystallized a copper selenite Cu-L4 from copper(II) acetate monohydrate and sodium selenite by using hydrothermal method with ratio of 1:1. The structure was presented in three-dimensional framework. The new compound was in the cubic chiral space group $P2_13$. Copper centers were in square pyramids and trigonal bipyramids geometry. Moreover, Cu-L4 was obtained from the hydrothermal synthesis at 170 °C, which was lower than chemical transport method from the literature. The complex from seleno-L-cystine ligand (L5) was not confirm the complexation because of the limitation of equipment. We needed other ways of crystallization and/or characterization to confirm this product.

REFERENCES

1. Furukawa, H.; Cordova, K. E.; O'Keeffe, M.; Yaghi, O. M., The chemistry and applications of metal-organic frameworks. *Science* **2013**, *341* (6149), 1230444-1-1230444-12.
2. Lalonde, M. B.; Farha, O. K.; Scheidt, K. A.; Hupp, J. T., N-heterocyclic carbene-like catalysis by a metal-organic framework material. *ACS Catalysis* **2012**, *2* (8), 1550-1554.
3. Jiao, C.; Zhang, J.; Wang, S.; Si, X.; You, W.; Li, Z.; Wang, Z.; Yu, H.; Gabelica, Z.; Zhou, H. Y.; Sun, L.; Xu, F., Polarized micropores in a novel 3D metal-organic framework for selective adsorption properties. *Inorg Chem* **2012**, *51* (9), 5022-5025.
4. Usman, M.; Mendiratta, S.; Batjargal, S.; Haider, G.; Hayashi, M.; Rao Gade, N.; Chen, J. W.; Chen, Y. F.; Lu, K. L., Semiconductor behavior of a three-dimensional strontium-based metal-organic framework. *ACS Appl Mater Interfaces* **2015**, *7* (41), 22767-22774.
5. Zhao, X.; Bu, X.; Wu, T.; Zheng, S. T.; Wang, L.; Feng, P., Selective anion exchange with nanogated isorecticular positive metal-organic frameworks. *Nat Commun* **2013**, *4*, 1-9.
6. Yan, Z.-Q.; Meng, X.-T.; Su, R.-R.; Zeng, C.-H.; Yang, Y.-Y.; Zhong, S.; Ng, S. W., Basophilic method for lanthanide MOFs with a drug ligand: Crystal structure and luminescence. *Inorganica Chimica Acta* **2015**, *432*, 41-45.
7. Ke, F.; Qiu, L.-G.; Yuan, Y.-P.; Jiang, X.; Zhu, J.-F., Fe₃O₄@MOF core-shell magnetic microspheres with a designable metal-organic framework shell. *Journal of Materials Chemistry* **2012**, *22* (19), 9497-9500.
8. Horcajada, P.; Serre, C.; Vallet-Regi, M.; Sebban, M.; Taulelle, F.; Ferey, G., Metal-organic frameworks as efficient materials for drug delivery. *Angew Chem Int Ed Engl* **2006**, *45* (36), 5974-5978.

9. Horcajada, P.; Gref, R.; Baati, T.; Allan, P. K.; Maurin, G.; Couvreur, P.; Ferey, G.; Morris, R. E.; Serre, C., Metal-organic frameworks in biomedicine. *Chem Rev* **2012**, *112* (2), 1232-1268.
10. Horcajada, P.; Serre, C.; Maurin, G.; Ramsahye, N. A.; Balas, F.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Ferey, G., Flexible porous metal-organic frameworks for a controlled drug delivery. *J Am Chem Soc* **2008**, *130*, 6774-6780.
11. An, J.; Geib, S. J.; Rosi, N. L., Cation-triggered drug release from a porous zinc-adeninate metal-organic framework. *J Am Chem Soc Comm* **2009**, *131*, 8376-8377.
12. He, C.; Lu, K.; Liu, D.; Lin, W., Nanoscale metal-organic frameworks for the co-delivery of cisplatin and pooled siRNAs to enhance therapeutic efficacy in drug-resistant ovarian cancer cells. *J Am Chem Soc* **2014**, *136* (14), 5181-5184.
13. Hu, Q.; Yu, J.; Liu, M.; Liu, A.; Dou, Z.; Yang, Y., A low cytotoxic cationic metal-organic framework carrier for controllable drug release. *J Med Chem* **2014**, *57* (13), 5679-5685.
14. Ma, D. Y.; Li, Z.; Xiao, J. X.; Deng, R.; Lin, P. F.; Chen, R. Q.; Liang, Y. Q.; Guo, H. F.; Liu, B.; Liu, J. Q., Hydrostable and nitryl/methyl-functionalized metal-organic framework for drug delivery and highly selective CO₂ adsorption. *Inorg Chem* **2015**, *54* (14), 6719-6726.
15. Sarquis, M.; Mickey, C. D., Selenium. Part 1: Its chemistry and occurrence. *J. Chem. Educ.* **1980**, *57* (12), 886-889.
16. Kimani, M. M.; Bayse, C. A.; Stadelman, B. S.; Brumaghim, J. L., Oxidation of biologically relevant chalcogenones and their Cu(I) complexes: Insight into selenium and sulfur antioxidant activity. *Inorganic Chemistry* **2013**, *52* (20), 11685-11687.
17. Deng, Z.; Yu, L.; Cao, W.; Zheng, W.; Chen, T., A selenium-containing ruthenium complex as a cancer radiosensitizer, rational design and the important role of ROS-mediated signalling. *Chem Commun (Camb)* **2015**, *51* (13), 2637-40.
18. Li, T.; Smet, M.; Dehaen, W.; Xu, H., Selenium-platinum coordination dendrimers with controlled anti-cancer activity. *ACS Appl Mater Interfaces* **2016**, *8* (6), 3609-14.

19. Xavier, A.; Srividhya, N., Synthesis and study of schiff base ligands. *IOSR-JAC* **2014**, 7 (11), 6-15.
20. Sarvari, M. H.; Sharghi, H., Reactions on a solid surface. A simple, economical and efficient friedel–crafts acylation reaction over zinc oxide (ZnO) as a new catalyst. *The Journal of Organic Chemistry* **2004**, 69 (20), 6953-6956.
21. Banerjee, D.; Kim, S. J.; Parise, J. B., Lithium based metal–organic framework with exceptional stability. *Crystal Growth & Design* **2009**, 9 (5), 2500-2503.
22. Canossa, S.; Bellè, E.; Delferro, M.; Predieri, G.; Graiff, C., Structural motifs in heteroleptic copper and cadmium selenites. *Inorganica Chimica Acta* **2018**, 470, 206-212.
23. Meunier, G.; Bertaud, M., Constantes cristallographiques de CuSe_2O_5 , CuSeO_3 et Cu_2SeO_4 . *Journal of Applied Crystallography* **1976**, 9 (4), 364-366.
24. Ferraro, J. R.; Walker, W. R., Infrared spectra of hydroxy-bridged copper(II) compounds. *Inorganic Chemistry* **1965**, 4 (10), 1382-1386.





APPENDIX

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Table A.1 Experimental details

Crystal data

Chemical formula	0.25(Cu ₁₆ O ₃₂ Se ₈)
M_r	540.08
Crystal system, space group	Cubic, $P2_13$
Temperature (K)	296
a (Å)	8.9223 (3)
V (Å ³)	710.28 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	22.08
Crystal size (mm)	0.26 × 0.22 × 0.22

Data collection

Diffractometer	Bruker D8 QUEST CMOS
Absorption correction	Multi-scan

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SADABS2016/2 (Bruker,2016/2) was used for absorption correction. $wR2(\text{int})$ was 0.1383 before and 0.0649 after correction. The Ratio of minimum to maximum transmission is 0.6962. The $\lambda/2$ correction factor is Not present.

T_{\min}, T_{\max}	0.520, 0.746
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No. of measured,
independent and
observed [$I > 2\sigma(I)$]
reflections

27056, 822, 795

 R_{int}

0.042

 $(\sin \theta/\lambda)_{\text{max}}$ (\AA^{-1})

0.739

Refinement

 $R[F2 > 2\sigma(F^2)], wR(F^2), S$

0.014, 0.027, 1.23

No. of reflections

822

No. of parameters

44

 $\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})

0.71, -0.48

Absolute structure

Flack x determined using 326 quotients [(+)-
(-)]/[(+)+(-)]

Absolute structure parameter

0.014 (7)

Table A.2 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Se1	1.21109 (3)	0.28891 (3)	0.71109 (3)	0.00565 (11)
Se2	0.54133 (4)	0.54133 (4)	0.54133(4)	0.00666 (11)
Cu1	0.87175 (5)	0.36652 (5)	0.62106 (5)	0.00605 (8)
Cu2	0.88616 (5)	0.61384 (5)	0.38616 (5)	0.00878 (14)
O1	1.0320 (3)	0.2294 (3)	0.6871 (3)	0.0095 (4)
O2	0.7297 (3)	0.5179 (3)	0.5314 (3)	0.0163 (5)
O3	1.0106 (3)	0.4894 (3)	0.5106 (3)	0.0064 (9)
O4	0.7627 (3)	0.7373 (3)	0.2627 (3)	0.0053 (8)

Table A.3 Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Se1	0.00565 (11)	0.00565 (11)	0.00565 (11)	0.00064 (11)	-0.00064 (11)	0.00064 (11)
Se2	0.00666 (11)	0.00666 (11)	0.00666 (11)	0.00065 (12)	0.00065 (12)	0.00065 (12)
Cu1	0.00508 (17)	0.00608 (17)	0.00700 (18)	-0.00004 (13)	0.00079 (14)	0.00162 (14)
Cu2	0.00878 (14)	0.00878 (14)	0.00878 (14)	0.00177 (15)	-0.00177 (15)	0.00177 (15)
O1	0.0055 (10)	0.0085 (10)	0.0144 (11)	-0.0010 (9)	-0.0006 (9)	0.0031 (9)
O2	0.0071 (11)	0.0196 (12)	0.0223 (13)	0.0071 (9)	0.0080 (10)	0.0132 (11)
O3	0.0064 (9)	0.0064 (9)	0.0064 (9)	0.0005 (8)	-0.0005 (8)	0.0005 (8)
O4	0.0053 (8)	0.0053 (8)	0.0053 (8)	0.0005 (7)	-0.0005 (7)	0.0005 (7)

Table A.4 Geometric parameters (Å, °)

Se1—O1 ⁱ	1.697 (2)	Cu1—O2	2.018 (2)
Se1—O1 ⁱⁱ	1.697 (2)	Cu1—O3	1.9258 (11)
Se1—O1	1.697 (2)	Cu1—O4 ^{vi}	1.9737 (19)
Se2—O2 ⁱⁱⁱ	1.696 (2)	Cu2—O2 ⁱ	2.088 (2)
Se2—O2 ^{iv}	1.696 (2)	Cu2—O2 ⁱⁱ	2.088 (2)
Se2—O2	1.696 (2)	Cu2—O2	2.088 (2)
Cu1—O1 ^v	2.29 (2)	Cu2—O3	1.922 (4)
Cu1—O1	1.972 (2)	Cu2—O4	1.907 (4)
O1 ⁱ —Se1—O1 ⁱⁱ	102.42 (9)	O4—Cu2—O2 ⁱⁱ	102.06 (7)
O1 ⁱ —Se1—O1	102.42 (9)	O4—Cu2—O2	102.06 (7)
O1 ⁱⁱ —Se1—O1	102.42 (9)	O4—Cu2—O2 ⁱ	102.06 (7)
O2—Se2—O2 ^{iv}	99.63 (14)	O4—Cu2—O3	180 (7)
O2 ⁱⁱⁱ —Se2—O2 ^{iv}	99.63 (14)	Se1—O1—Cu1	121.76 (13)
O2—Se2—O2 ⁱⁱⁱ	99.63 (14)	Se1—O1—Cu1 ^{vii}	126.63 (12)
O1—Cu1—O1 ^v	91.75 (13)	Cu1—O1—Cu1 ^{vii}	91.19 (9)
O1—Cu1—O2	171.61 (10)	Se2—O2—Cu1	133.16 (14)
O1—Cu1—O4 ^{vi}	87.62 (10)	Se2—O2—Cu2	130.14 (13)
O2—Cu1—O1 ^v	89.08 (10)	Cu1—O2—Cu2	95.77 (10)
O3—Cu1—O1 ^v	110.26 (7)	Cu1 ⁱ —O3—Cu1	113.82 (9)
O3—Cu1—O1	92.28 (13)	Cu1 ⁱ —O3—Cu1 ⁱⁱ	113.82 (9)
O3—Cu1—O2	79.61 (13)	Cu1—O3—Cu1 ⁱⁱ	113.82 (9)
O3—Cu1—O4 ^{vi}	170.43 (8)	Cu2—O3—Cu1 ⁱⁱ	104.66 (12)
O4 ^{vi} —Cu1—O1 ^v	79.3 (9)	Cu2—O3—Cu1	104.66 (12)
O4 ^{vi} —Cu1—O2	100.74 (10)	Cu2—O3—Cu1 ⁱ	104.66 (12)
O2 ⁱ —Cu2—O2	115.76 (5)	Cu1 ^{viii} —O4—Cu1 ^{iv}	101.32 (13)
O2 ⁱⁱ —Cu2—O2	115.76 (5)	Cu1 ^{ix} —O4—Cu1 ^{iv}	101.32 (13)
O2 ⁱ —Cu2—O2 ⁱⁱ	115.76 (5)	Cu1 ^{viii} —O4—Cu1 ^{ix}	101.32 (13)
O3—Cu2—O2	77.94 (7)	Cu2—O4—Cu1 ^{iv}	116.74 (11)

$O3-Cu2-O2^i$	77.94 (7)	$Cu2-O4-Cu1^{viii}$	116.74 (11)
$O3-Cu2-O2^{ii}$	77.94 (7)	$Cu2-O4-Cu1^{ix}$	116.74 (11)

Symmetry codes: (i) $z+1/2, -x+3/2, -y+1$; (ii) $-y+3/2, -z+1, x-1/2$; (iii) y, z, x ; (iv) z, x, y ; (v) $-y+1, z-1/2, -x+3/2$; (vi) $-x+3/2, -y+1, z+1/2$; (vii) $-z+3/2, -x+1, y+1/2$; (viii) $-x+3/2, -y+1, z-1/2$; (ix) $y+1/2, -z+3/2, -x+1$.



VITA

I am Sakvarit Nitrathorn, master degree student in Department of Chemistry, Faculty of Science, Chulalongkorn University. I had graduated the bachelor degree in Science, major in Chemistry from Faculty of Science, Chulalongkorn University. I got the opportunity to attend the dual degree program, which is the collaboration program between Chulalongkorn University and Japan Advanced Institute of Science and Technology (Nomi, Ishikawa, Japan) or JAIST. My research topic at JAIST is PREPARATION, STABILITY, AND PHOTOELECTROCHEMICAL PROPERTY STUDY OF COPPER-BRIDGED PORPHYRINATOCOBALT(II) THIN FILM.





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