

## CHAPTER 2

### EXPERIMENTS

#### 2.1 Chemicals and reagents

The chemicals and reagents were used without any purification or pretreatment unless specified otherwise. The chemicals and reagents are shown in Table 1.

**Table 1** Chemicals and reagents

Number	Chemicals	Sources	Grade	Remarks
1	Copper(I) chloride	Fluka	Analytical	Switzerland
2	Copper(I) bromide	Fluka	Analytical	Switzerland
3	Copper(I) iodide	Fluka	Analytical	Switzerland
4	Copper nitrate trihydrate	Fluka	Chemika	Switzerland
5	<i>N,N'</i> -diphenylthiourea (dptu)	Fluka	Analytical	Switzerland
6	<i>N</i> -phenylthiourea (ptu)	Fluka	Analytical	Switzerland
7	<i>N,N'</i> -ethylenethiourea (etu)	Fluka	Analytical	Switzerland

**Table 1** (Continued)

Number	Chemicals	Sources	Grade	Remarks
8	$[\text{Cu}(\text{dptu})_2\text{Cl}]\text{H}_2\text{O}$	Synthesized by Asst. Prof. Dr. Chaveng's research group		PSU, Thailand
9	$[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$	Synthesized by Asst. Prof. Dr. Chaveng's research group		PSU, Thailand
10	$[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$	Synthesized by Asst. Prof. Dr. Chaveng's research group		PSU, Thailand
11	$[\text{Cu}(\text{ptu})_4]\text{Cl}$	Synthesized		
12	$[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$	Synthesized		
13	$[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$	Synthesized		
14	$[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$	Synthesized		
15	$[\text{Cu}(\text{etu})_3\text{Br}]$	Synthesized		
16	$[\text{Cu}_2(\text{etu})_4\text{I}_2]$	Synthesized		
17	Acetonitrile	LAB-SCAN	Analytical	Ireland
18	Tetrabutylammonium hexafluorophosphate	Fluka	Electrochemical	Switzerland

**Table 1** (Continued)

Number	Chemicals	Sources	Grade	Remarks
19	Alumina powder	Buehler	0.05 micron diameter	USA
20	Tetrabutylammonium chloride	Fluka	Analytical	Switzerland
21	Tetrabutylammonium bromide	Fluka	Analytical	Switzerland
22	Tetrabutylammonium iodide	Fluka	Analytical	Switzerland

The reagents were prepared according to the methods and calculations specified in details in the Appendix B.

## 2.2 Instruments

2.2.1 Capillary melting point apparatus, Thomas Hoover, Unimelt 0-360 °C

2.2.2 Thermometer, Gallenkamp, England 0-360 °C

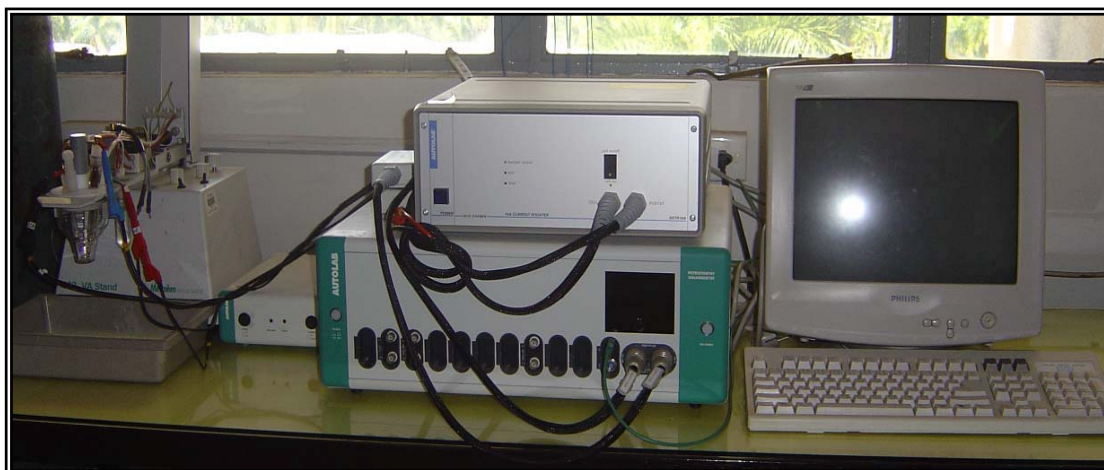
2.2.3 Hot plate stirrer with magnetic bar

2.2.4 Vacuum desiccator

2.2.5 Electrochemical apparatus and electrodes

All the measurements were performed with a conventional three-electrode configuration. The working electrode was a glassy carbon electrode, GCE (2 millimeter diameter), polished with alumina (0.05  $\mu$ ) water slurry on polishing cloth, rinsed well with distilled water and wiped several times with wetted soft tissue. The counter electrode was a platinum wire and an Ag/AgCl/KCl<sub>sat</sub> electrode was used as the reference electrode for cyclic voltammetry. All electrodes are from Metrohm, Switzerland. Cyclic voltammetric data were

recorded using a computer - controlled potentiostat/galvanostat (AUTOLAB PGSTAT 100, Metrohm, Switzerland).



**Figure 11** The electrochemical apparatus, AUTOLAB PGSTAT 100 (Metrohm, Switzerland)



**Figure 12** The three electrode system in the electrochemical cell

## 2.3 Procedure

### 2.3.1 Preparation of complexes

#### 2.3.1.1 Preparation of $[\text{Cu}(\text{dptu})_2\text{Cl}]\text{H}_2\text{O}$ complex

A 2.2831-g of *N,N'*-diphenylthiourea ( $1.0 \times 10^{-2}$  mole, Appendix 3.2 ) was dissolved in 100 ml of acetonitrile at  $60^\circ\text{C}$ . Then a 0.4950-g of  $\text{CuCl}$  ( $5.0 \times 10^{-3}$  mole, Appendix 4.2) was slowly added with continuous stirring for 3 hrs. After that it was filtered and the filtrate was left at room temperature. After 1 day, slow evaporation of this solution yielded crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.2 Preparation of $[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$ complex

A 1.1416-g of *N,N'*-diphenylthiourea ( $5.0 \times 10^{-3}$  mole, Appendix 3.3 ) was dissolved in 80 ml of acetonitrile at  $60^\circ\text{C}$ . Then a 0.3586-g of  $\text{CuBr}$  ( $2.5 \times 10^{-3}$  mole, Appendix 4.3) was slowly added with continuous stirring for 4 hrs. After that, it was filtered and the filtrate was left at room temperature. Slow evaporation of this solution yielded crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.3 Preparation of $[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$ complex

A 1.3699-g of *N,N'*-diphenylthiourea ( $6.0 \times 10^{-3}$  mole, Appendix 3.4 ) was dissolved in 80 ml of acetonitrile at  $60^\circ\text{C}$ . Then a 0.5713-g of  $\text{CuI}$  ( $3.0 \times 10^{-3}$  mole, Appendix 4.6) was slowly added with continuous stirring for 3 hrs. After that, it was filtered and the filtrate was left at room temperature. Slow evaporation of this solution yielded crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.4 Preparation of $[\text{Cu}(\text{ptu})_4]\text{Cl}$ complex

A 2.300-g of *N*-phenylthiourea ( $1.5 \times 10^{-4}$  mole, Appendix 3.7) was dissolved in 60 ml of acetonitrile at  $50^\circ\text{C}$  with continuous stirring. A 0.4950-g of  $\text{CuCl}$  ( $5.0 \times 10^{-3}$  mole, Appendix 4.2) was slowly added and the solution was kept warm for 5 hrs. After that, it was

filtered and the filtrate was then left at room temperature. Slow evaporation of this solution yielded colorless crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.5 Preparation of $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$ complex

A 1.600-g of *N*-phenylthiourea ( $1.0 \times 10^{-4}$  mole, Appendix 3.6) was dissolved in 60 ml of acetonitrile at  $60^\circ\text{C}$  with continuous stirring. A 0.5020-g of CuBr ( $3.5 \times 10^{-3}$  mole, Appendix 4.4) was slowly added and the solution was kept warm for 4 hrs. After that, it was filtered and the filtrate was then left at room temperature. Slow evaporation of this solution yielded colorless plate crystals. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.6 Preparation of $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$ complex

A 1.1900-g of *N*-phenylthiourea ( $2.6 \times 10^{-3}$  mole, Appendix 3.8) was dissolved in 60 ml of acetonitrile at  $60^\circ\text{C}$  with continuous stirring. A 1.4855-g of CuI ( $7.8 \times 10^{-3}$  mole, Appendix 4.8) was slowly added and the solution was kept warm for 4 hrs. After that, it was filtered and the filtrate was then left at room temperature. After 2 days, colorless plate crystals were obtained. They were isolated by suction filtration and washed with acetone before being dried in a vacuum desiccator.

#### 2.3.1.7 Preparation of $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$ complex

A 4.3400-g of *N,N'*-ethylenethiourea ( $4.3 \times 10^{-2}$  mole, Appendix 3.11) was dissolved in 100 ml of distilled water at  $50^\circ\text{C}$  with continuous stirring. A 1.4850-g of CuCl ( $1.5 \times 10^{-2}$  mole, Appendix 4.1) was slowly added and the solution was kept warm for 30 min. After that, it was filtered by suction filtration and the filtrate then left at room temperature. Slow evaporation of this solution yielded colorless crystals. They were isolated by suction filtration and dried in an oven at  $50^\circ\text{C}$ .

### 2.3.1.8 Preparation of [Cu(etu)<sub>3</sub>Br] complex

A 1.2258-g of *N,N'*-ethylenethiourea ( $8.0 \times 10^{-4}$  mole, Appendix 3.10) was dissolved in 60 ml of distilled water at room temperature with continuous stirring. A 0.5738-g of CuBr ( $4.0 \times 10^{-3}$  mole, Appendix 4.5) was slowly added and the solution with continuous stirring for 1 hrs. After that, it was filtered by suction filtration. Slow evaporation of this solution was allowed by leaving the filtrate at room temperature. After 2 days, colorless plate crystals were obtained. They were isolated by suction filtration and dried.

### 2.3.1.9 Preparation of [Cu<sub>2</sub>(etu)<sub>4</sub>I<sub>2</sub>] complex

A 0.8173-g of *N,N'*-ethylenethiourea ( $8.0 \times 10^{-3}$  mole, Appendix 3.12) was dissolved in 50 ml of distilled water at room temperature with continuous stirring. A 0.7618-g of CuI ( $4.0 \times 10^{-3}$  mole, Appendix 4.7) was slowly added and the solution with continuous stirring for 1 hrs. After that, it was filtered by suction filtration. Slow evaporation of this solution was allowed by leaving the filtrate at room temperature. After 7 days, the solution yielded crystals. They were isolated by suction filtration and dried.

## 2.3.2 Electrochemical procedures

### 2.3.2.1 Cyclic voltammetry of the blank solution

A 25-ml of acetonitrile (CH<sub>3</sub>CN) solution was pipetted into the cell with a 0.9686-g of tetrabutylammonium hexafluorophosphate (0.1 M, TBAP, Appendix 1.1) in a three electrode system consisting of glassy carbon electrode (GCE) as a working electrode, platinum wire as a counter electrode and a Ag/AgCl/KCl<sub>sat</sub> electrode as the reference electrode. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential.

### 2.3.2.2 Cyclic voltammetry of copper ions

After the cyclic voltammetry of blank was recorded, 0.01 M of copper(II) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from positive potential to negative potential between -1.75 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

### 2.3.2.3 Cyclic voltammetry of halide ions

#### a) Cyclic voltammetry of chloride ion

After the cyclic voltammetry of blank was recorded, a 0.069-g (0.01M) of tetrabutylammonium chloride (Appendix 2.1) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative potential to positive potential between -0.25 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

#### b) Cyclic voltammetry of bromide ion

After the cyclic voltammetry of blank was recorded, a 0.081-g (0.01 M) of tetrabutylammonium bromide (Appendix 2.2) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative potential to positive potential between -1.50 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

#### c) Cyclic voltammetry of iodide ion

After the cyclic voltammetry of blank was recorded, a 0.092-g (0.01 M) of tetrabutylammonium iodide (Appendix 2.3) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -1.00 to 1.50 V vs Ag/AgCl electrode with 2 potential cycles.



#### 2.3.2.4 Cyclic voltammetry of substituted thioureas

##### a) Cyclic voltammetry of *N,N'*-diphenylthiourea

After the cyclic voltammetry of blank was recorded, a 0.5708-g (0.1 M) of *N,N'*-diphenylthiourea (Appendix 3.1) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

##### b) Cyclic voltammetry of *N*-phenylthiourea

After the cyclic voltammetry of blank was recorded, a 0.3804-g (0.1 M) of *N*-phenylthiourea (Appendix 3.5) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

##### c) Cyclic voltammetry of *N,N'*-ethylenethiourea

After the cyclic voltammetry of blank was recorded, a 0.2553-g (0.1 M) of *N,N'*-ethylenethiourea (Appendix 3.9) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

#### 2.3.2.5 Cyclic voltammetry of Cu(I) halide with *N,N'*-diphenylthiourea complex

##### a) Cyclic voltammetry of [Cu(dptu)<sub>2</sub>Cl]H<sub>2</sub>O complex

After the cyclic voltammetry of blank was recorded, a 0.0143-g (0.001 M) of [Cu(dptu)<sub>2</sub>Cl]H<sub>2</sub>O complex (Appendix 5.1) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

b) Cyclic voltammetry of  $[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$  complex

After the cyclic voltammetry of blank was recorded, a 0.0154-g (0.001 M) of  $[\text{Cu}(\text{dptu})_2\text{Br}]\text{H}_2\text{O}$  complex (Appendix 5.2) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

c) Cyclic voltammetry of  $[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$  complex

After the cyclic voltammetry of blank was recorded, a 0.0166-g (0.001 M) of  $[\text{Cu}(\text{dptu})_2\text{I}]\text{H}_2\text{O}$  complex (Appendix 5.3) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.50 V vs Ag/AgCl electrode with 2 potential cycles.

### 2.3.2.6 Cyclic voltammetry of Cu(I) halide with *N*- phenylthiourea complexes

a) Cyclic voltammetry of  $[\text{Cu}(\text{ptu})_4]\text{Cl}$  complex

After the cyclic voltammetry of blank was recorded, a 0.0177-g (0.001 M) of  $[\text{Cu}(\text{ptu})_4]\text{Cl}$  complex (Appendix 6.1) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

b) Cyclic voltammetry of  $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$  complex

After the cyclic voltammetry of blank was recorded, a 0.0744-g (0.001 M) of  $[\text{Cu}_4(\text{ptu})_6\text{Br}_4]_2$  complex (Appendix 6.2) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

c) Cyclic voltammetry of  $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$  complex

After the cyclic voltammetry of blank was recorded, a 0.0837-g (0.001 M) of  $[\text{Cu}_4(\text{ptu})_6\text{I}_4]_2$  complex (Appendix 6.3) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.50 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

### 2.3.2.7 Cyclic voltammetry of Cu(I) halide with *N,N'*-ethylenethiourea complex

a) Cyclic voltammetry of  $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$  complex

After the cyclic voltammetry of blank was recorded, a 0.0152-g (0.001 M) of  $[\text{Cu}_2(\text{etu})_4\text{Cl}_2]$  complex (Appendix 7.1) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.00 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

b) Cyclic voltammetry of  $[\text{Cu}(\text{etu})_3\text{Br}]$  complex

After the cyclic voltammetry of blank was recorded, a 0.0112-g (0.001 M) of  $[\text{Cu}(\text{etu})_3\text{Br}]$  complex (Appendix 7.2) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.00 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.

c) Cyclic voltammetry of  $[\text{Cu}_2(\text{etu})_4\text{I}_2]$  complex

After the cyclic voltammetry of blank was recorded, a 0.0150-g (0.001 M) of  $[\text{Cu}_2(\text{etu})_4\text{I}_2]$  complex (Appendix 7.3) was added in blank solution. Nitrogen gas was purged for 3 min to eliminate interfering oxygen. Voltammograms were then recorded by scanning from negative to positive potential between -2.00 to 2.00 V vs Ag/AgCl electrode with 2 potential cycles.