APPENDIX A

1. **The bond distances of copper with halides in various of *N,N'*-diphenylthiourea, *N*-phenylthiourea and *N,N'*-ethylenethiourea complexes** (Pakawatchai, 1990., Singhagomol, 1999. and Tanchatchawal, 2004.)

Complexes	The bond distances of copper with halides	
	Type of bond	The bond distances (°A)
$[Cu(dptu)_2Cl]H_2O$	Cu-Cl	2.221
$[Cu(dptu)_2Br]H_2O$	Cu-Br	2.3695
$[Cu(dptu)_2I]H_2O$	Cu-I	2.5209
$[Cu(ptu)_4]Cl$	Cu-Cl	-
$[Cu_4(ptu)_6Br_4]_2$	Cu-Br	2.478-2.496
$[Cu_4(ptu)_6I_4]_2$	Cu-I	2.627-2.746
$[Cu(etu)_2Cl]_2$	Cu-Cl	2.2781-2.3310
$[Cu(etu)_3Br]$	Cu-Br	2.488
$[Cu_2(etu)_4I_2]$	Cu-I	2.552

2. The bond distances of intramolecular hydrogent, NH-halide in various of *N,N′*-diphenylthiourea complexes (Singhagomol, 1999.**)**

Complexes	The bond distances of intramolecular hydrogent, NH-halide (°A)
$[Cu(dptu)_2Cl]H_2O$	2.4600, 2.7179
$[Cu(dptu)_2Br]H_2O$	2.6178, 2.7576
$[Cu(dptu)_2I]H_2O$	2.9171, 2.9564

3. The bond distances of copper with sulfur in various of *N,N′*-diphenylthiourea, *N*-phenylthiourea and *N,N′*-ethylenethiourea complexes (Pakawatchai, 1990., Singhagomol, 1999. and Tanchatchawal, 2004.)

Complexes	The bond distances of Cu-S (°A)
$[Cu(dptu)_2Cl]H_2O$	2.207-2.227
$[Cu(dptu)_2Br]H_2O$	2.2298-2.2311
$[Cu(dptu)_2I]H_2O$	2.2305-2.2391
$[Cu(ptu)_4]Cl$	2.335
$[Cu_4(ptu)_6Br_4]_2$	2.261-2.352
$[Cu_4(ptu)_6I_4]_2$	2.283-2.421
$[Cu(etu)_2Cl]_2$	2.2084-2.6470
$[Cu(etu)_3Br]$	(*)
$[Cu_2(etu)_4I_2]$	(*)

Remarks: (*) = No data

APPENDIX B

1. Calculationsof the concentration of supporting electrolyte

1.1 Preparation of 0.1 M tetrabutylammonium hexafluorophosphate

Mw = 387.43 g/mol

V = 25×10^{-3} L

M = 0.1 mol/L

m (g) = Mw x V x M

= (387.43 g/mol) x (25×10^{-3} L) x (0.1 mol/L)

= 0.9686 g

Therefore, weigh TBAP 0.9686 g and dissolve in CH_3CN 25 ml.

2. Calculations of the concentration of halide ions

2.1 Preparation of 0.01 M tetrabutylammonium chloride

Mw = 277.92 g/mol

V = 25×10^{-3} L

M = 0.01 mol/L

m (g) = Mw x V x M

= (277.92 g/mol) x (25×10^{-3} L) x (0.01 mol/L)

= 0.069 g

Therefore, weigh tetrabutylammonium chloride 0.069 g and dissolve in CH_3CN 25 ml.

2.2 Preparation of 0.01 M tetrabutylammonium bromide

Mw = 322.37 g/mol

V = 25×10^{-3} L

M = 0.01 mol/L

m (g) = Mw x V x M

= (322.37 g/mol) x (25×10^{-3} L) x (0.01 mol/L)

= 0.081 g

Therefore, weigh tetrabutylammonium bromide 0.081 g and dissolve in CH_3CN 25 ml.

2.3 Preparation of 0.01 M tetrabutylammonium iodide

Mw = 369.37 g/mol

V = 25×10^{-3} L

M = 0.01 mol/L

m (g) = Mw x V x M

= (369.37 g/mol) x (25×10^{-3} L) x (0.01 mol/L)

= 0.092 g

Therefore, weigh tetrabutylammonium iodide 0.092 g and dissolve in CH_3CN 25 ml.

3. Calculations of the concentration of substituted thioureas

3.1 Preparation of 0.1 M *N,N'*-diphenylthioureas (dptu)

Mw = 228.31 g/mol

V = 25×10^{-3} L

M = 0.1 mol/L

m (g) = Mw x V x M

= (228.31 g/mol) x (25×10^{-3} L) x (0.1 mol/L)

= 0.5708 g

Therefore, weigh dptu 0.5708 g and dissolve in CH_3CN 25 ml.

3.2 Preparation of 1.0 x 10^{-2} mole *N,N′*-diphenylthioureas (dptu)

Mw = 228.31 g/mol

N,N′-diphenylthioureas 1 mole = 228.31 g

N,N′-diphenylthioureas 1 x 10^{-2} mole = (228.31 x 1 x 10^{-2}) / 1 g

N,N′-diphenylthioureas 1 x 10^{-2} mole = 2.2831 g

3.3 Preparation of 5.0 x 10^{-3} mole *N,N′*-diphenylthioureas (dptu)

Mw = 228.31 g/mol

N,N′-diphenylthioureas 1 mole = 228.31 g

N,N′-diphenylthioureas 5.0 x 10^{-3} mole = (228.31 x 5.0 x 10^{-3}) / 1 g

N,N′-diphenylthioureas 5.0 x 10^{-3} mole = 1.1416 g

3.4 Preparation of 6.0 x 10^{-3} mole *N,N′*-diphenylthioureas (dptu)

Mw = 228.31 g/mol

N,N′-diphenylthioureas 1 mole = 228.31 g

N,N′-diphenylthioureas 6.0 x 10^{-3} mole = (228.31 x 6.0 x 10^{-3}) / 1 g

N,N′-diphenylthioureas 6.0 x 10^{-3} mole = 1.3699 g

3.5 Preparation of 0.1 M *N*-phenylthioureas (ptu)

Mw = 152.15 g/mol

V = 25x 10^{-3} L

M = 0.1 mol/L

m (g) = Mw x V x M

= (152.15 g/mol) x (25x 10^{-3} L) x (0.1 mol/L)

= 0.3804 g

Therefore, weigh ptu 0.380 g and dissolve in CH_3CN 25 ml.

3.6 Preparation of 1.0 x 10^{-2} mole *N*-phenylthioureas (ptu)

Mw = 152.15 g/mol

N-phenylthioureas 1 mole = 152.15 g

N-phenylthioureas 1 x 10^{-2} mole = (152.15 x 1 x 10^{-4}) / 1 g

N-phenylthioureas 1 x 10^{-2} mole = 1.5220 g

3.7 Preparation of 1.5 x 10^{-2} mole *N*-phenylthioureas (ptu)

Mw = 152.15 g/mol

N-phenylthioureas 1 mole = 152.15 g

N-phenylthioureas 1.5 x 10^{-2} mole = (152.15 x 1.5 x 10^{-2}) / 1 g

N-phenylthioureas 1.5 x 10^{-2} mole = 2.2823 g

3.8 Preparation of 2.6 x 10^{-3} mole *N*-phenylthioureas (ptu)

Mw = 152.15 g/mol

N-phenylthioureas 1 mole = 152.15 g

N-phenylthioureas 2.6 x 10^{-3} mole = (152.15 x 2.6 x 10^{-3}) / 1 g

N-phenylthioureas 2.6 x 10^{-3} mole = 0.3956 g

3.9 Preparation of 0.1 M *N,N'*-ethylenethiourea (etu)

Mw = 102.11 g/mol

V = 25x 10^{-3} L

M = 0.1 mol/L

m (g) = Mw x V x M

= (102.11 g/mol) x (25 x 10^{-3} L) x (0.1 mol/L)

= 0.2553 g

Therefore, weigh etu 0.2553 g and dissolve in CH_3CN 25 ml.

3.10 Preparation of 1.2 x 10^{-2} mole *N,N′*-ethylenethiourea (etu)

Mw = 102. g/mol

N,N′-ethylenethiourea 1 mole = 102.11 g

N,N′-ethylenethiourea 1.2 x 10^{-2} mole = (102.11 x 1.2 x 10^{-2}) / 1 g

N,N′-ethylenethiourea 1.2 x 10^{-2} mole = 1.2253 g

3.11 Preparation of 4.3 x 10^{-2} mole *N,N′*-ethylenethiourea (etu)

Mw = 102.11 g/mol

N,N′-ethylenethiourea 1 mole = 102.11 g

N,N′-ethylenethiourea 4.3 x 10^{-2} mole = (102.11 x 4.3 x 10^{-2}) / 1 g

N,N′-ethylenethiourea 4.3 x 10^{-2} mole = 4.3907 g

3.12 Preparation of 8.0 x 10^{-3} mole *N,N′*-ethylenethiourea (etu)

Mw = 102.11 g/mol

N,N′-ethylenethiourea 1 mole = 102.11 g

N,N′-ethylenethiourea 8.0 x 10^{-3} mole = (102.11 x 8.0 x 10^{-3}) / 1 g

N,N′-ethylenethiourea 8.0 x 10^{-3} mole = 0.8169 g

4. Calculations of the concentration of CuX (X = Cl, Br and I)

4.1 Preparation of 1.5 x 10^{-2} mole Copper (I) chloride (CuCl)

Mw = 98.999 g/mol

Copper (I) chloride 1 mole = 102.11 g

Copper (I) chloride 1.5 x 10^{-2} mole = (98.999 x 1.5 x 10^{-2}) / 1 g

Copper (I) chloride 1.5 x 10^{-2} mole = 1.4850 g

4.2 Preparation of 5×10^{-3} mole Copper (I) chloride (CuCl)

Mw = 98.999 g/mol

Copper (I) chloride 1 mole = 102.11 g

Copper (I) chloride 5×10^{-3} mole = $(98.999 \times 5 \times 10^{-3}) / 1$ g

Copper (I) chloride 5×10^{-3} mole = 0.4950 g

4.3 Preparation of 2.5×10^{-3} mole Copper (I) bromide (CuBr)

Mw = 143.45 g/mol

Copper (I) bromide 1 mole = 143.45 g

Copper (I) bromide 2.5×10^{-3} mole = $(143.45 \times 2.5 \times 10^{-3}) / 1$ g

Copper (I) bromide 2.5×10^{-3} mole = 0.3586 g

4.4 Preparation of 3.5×10^{-3} mole Copper (I) bromide (CuBr)

Mw = 143.45 g/mol

Copper (I) bromide 1 mole = 143.45 g

Copper (I) bromide 3.5×10^{-3} mole = $(143.45 \times 3.5 \times 10^{-3}) / 1$ g

Copper (I) bromide 3.5×10^{-3} mole = 0.5020 g

4.5 Preparation of 4×10^{-3} mole Copper (I) bromide (CuBr)

Mw = 143.45 g/mol

Copper (I) bromide 1 mole = 143.45 g

Copper (I) bromide 4×10^{-3} mole = $(143.45 \times 4 \times 10^{-3}) / 1$ g

Copper (I) bromide 4×10^{-3} mole = 0.5738 g

4.6 Preparation of 3×10^{-3} mole Copper (I) iodide (CuI)

Mw = 190.45 g/mol

Copper (I) iodide 1 mole = 190.45 g

Copper (I) iodide 3×10^{-3} mole = $(190.45 \times 3 \times 10^{-3}) / 1$ g

Copper (I) iodide 3×10^{-3} mole = 0.5713 g

4.7 Preparation of 4×10^{-3} mole Copper (I) iodide (CuI)

Mw = 190.45 g/mol

Copper (I) iodide 1 mole = 190.45 g

Copper (I) iodide 4×10^{-3} mole = $(190.45 \times 4 \times 10^{-3}) / 1$ g

Copper (I) iodide 4×10^{-3} mole = 0.7618 g

4.8 Preparation of 7.8×10^{-3} mole Copper (I) iodide (CuI)

Mw = 190.45 g/mol

Copper (I) iodide 1 mole = 190.45 g

Copper (I) iodide 7.8×10^{-3} mole = $(190.45 \times 7.8 \times 10^{-3}) / 1$ g

Copper (I) iodide 7.8×10^{-3} mole = 1.4855 g

5. Calculations of the concentration of Cu(I) halides with *N,N'*-diphenylthiourea complexes

5.1 Preparation of 1×10^{-3} M $[Cu(dptu)_2Cl]H_2O$ complex

Mw = 573.44 g/mol

V = 25×10^{-3} L

M = 1×10^{-3} mol/L

m (g) = Mw x V x M

= (573.44 g/mol) x (25×10^{-3} L) x (1×10^{-3} mol/L)

= 0.0143 g

Therefore, weigh $[Cu(dptu)_2Cl]H_2O$ 0.0143 g and dissolve in CH_3CN 25 ml.

5.2 Preparation of 1×10^{-3} M $[Cu(dptu)_2Br]H_2O$ complex

Mw = 617.89 g/mol

V = 25×10^{-3} L

M = 1×10^{-3} mol/L

m (g) = Mw x V x M

= (617.89 g/mol) x (25×10^{-3} L) x (1×10^{-3} mol/L)

= 0.0154 g

Therefore, weigh $[Cu(dptu)_2Br]H_2O$ 0.0154 g and dissolve in CH_3CN 25 ml.

5.3 Preparation of $1x10^{-3}$ M $[Cu(dptu)_2I]H_2O$ complex

Mw = 664.89 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$mol/L

m (g) = Mw x V x M

= (664.89 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$mol/L)

= 0.0166 g

Therefore, weigh $[Cu(dptu)_2I]H_2O$ 0.0166 g and dissolve in CH_3CN 25 ml.

6 Calculations of the concentration of Cu(I) halides with *N*-phenylthiourea complexes

6.1 Preparation of $1x10^{-3}$ M $[Cu(ptu)_4Cl]$ complex

Mw = 707.9 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$mol/L

m (g) = Mw x V x M

= (707.9 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$mol/L)

= 0.0177 g

Therefore, weigh $[Cu(ptu)_4Cl]$ 0.0177 g and dissolve in CH_3CN 25 ml.

6.2 Preparation of $1x10^{-3}$ M $[Cu_4(ptu)_6Br_4]_2$ complex

Mw = 2974.25 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$mol/L

m (g) = Mw x V x M

= (2974.25 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$mol/L)

= 0.0744 g

Therefore, weigh $[Cu_4(ptu)_6Br_4]_2$ 0.0744 g and dissolve in CH_3CN 25 ml.

6.3 Preparation of $1x10^{-3}$ M $[Cu_4(ptu)_6I_4]_2$ complex

Mw = 3349.64 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$ mol/L

m (g) = Mw x V x M

= (3349.64 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$ mol/L)

= 0.0837 g

Therefore, weigh $[Cu_4(ptu)_6I_4]_2$ 0.0837 g and dissolve in CH_3CN 25 ml.

7 Calculations of the concentration of Cu(I) halides with *N,N'*-ethylenethiourea complexes

7.1 Preparation of $1x10^{-3}$ M $[Cu_2(etu)_4Cl_2]$ complex

Mw = 606.438 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$ mol/L

m (g) = Mw x V x M

= (606.438 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$ mol/L)

= 0.0152 g

Therefore, weigh $[Cu_2(etu)_4Cl_2]$ 0.0152 g and dissolve in CH_3CN 25 ml.

7.2 Preparation of $1x10^{-3}$ M $[Cu(etu)_3Br]$ complex

Mw = 449.78 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$ mol/L

m (g) = Mw x V x M

= (449.78 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$ mol/L)

= 0.0112 g

Therefore, weigh $[Cu(etu)_3Br]$ 0.0112 g and dissolve in CH_3CN 25 ml.

7.3 Preparation of $1x10^{-3}$ M $[Cu_2(etu)_4I_2]$ complex

Mw = 598.89 g/mol

V = 25×10^{-3} L

M = $1x10^{-3}$ mol/L

m (g) = Mw x V x M

= (598.89 g/mol) x (25×10^{-3} L) x ($1x10^{-3}$ mol/L)

= 0.0150 g

Therefore, weigh $[Cu_2(etu)_4I_2]$ 0.0150 g and dissolve in CH_3CN 25 ml.

APPENDIX C

Presentations of this thesis

This research was published in abstract of 56th Annual Meeting of the International Society of Electrochemistry (ISE2005), 25-30 September 2005, BEXCO (Busan Exhibition and Convention Center), Busan, South Korea. With the topic of Electrochemistry of copper (I) halides and *N,N'*-diphenylthiourea complexes.

This research was poster presented of 32nd Congress on science and Technology of Thailand (STT.32), 10-12 October 2006, Queen Sirikit National Convention Center, Bangkok, Thailand. The poster presentation in the topic of Electrochemical properties of copper (I) halides and substituted thiourea complexes which is presented by Miss Rattiya Chuaysong.