

CHAPTER III

EXPERIMENTAL



3.1 Chemicals

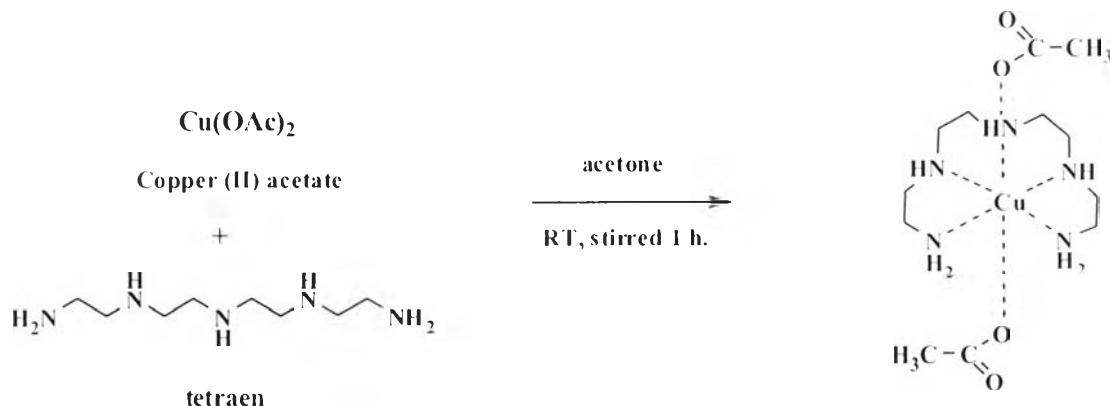
Copper (II) acetate monohydrate [Cu(OAc)₂.H₂O] was purchased from TCI Tokyo Kasei. Zinc (II) acetate dihydrate [Zn(OAc)₂.2H₂O], manganese (II) acetate tetrahydrate [Mn(OAc)₂.4H₂O], nickel (II) acetate tetrahydrate [Ni(OAc)₂.4H₂O], cobalt (II) acetate tetrahydrate [Co(OAc)₂.4H₂O], tetraethylenepentamine (tetraen), ethylenetriamine (en), triethylenetetramine (trien) were obtained from Fluka and Aldrich. Polymeric MDI (4,4'-methane diphenyl diisocyanate; PMDI, MR-200): %NCO = 31.0 (%wt.), average functionality = 2.7, Polyol (Raypol[®] 4221, sucrose-based polyether polyol), hydroxyl value (OHV) = 438.93 functionality = 4.3, Polysiloxane (TEGOSTAB B8460, Goldschmidt), N,N-dimethylcyclohexylamine (DMCHA) were supplied by Huntsman (Thailand) Co., Ltd. Distilled water was used as blowing agent.

3.2 Synthetic Procedures

Metal-amine and mixed metal-amine complexes were synthesized by different solvents. First, Acetone was used as a solvent in the synthesis of metal complexes [M(tetraen)]. Acetone was removed from metal complexes before using in the preparation of RPUR foam. Second, the preparation of metal complexes was done in distilled water to obtain an aqueous solution containing metal complexes [M(tetraen)-W]. The catalysts were used to prepare RPUR foam without purification. In this work, M(tetraen) and M(tetraen)-W were used as the codes for metal complexes synthesized in acetone and water, respectively.

3.2.1 Synthesis of Metal-Amine Complexes in Acetone

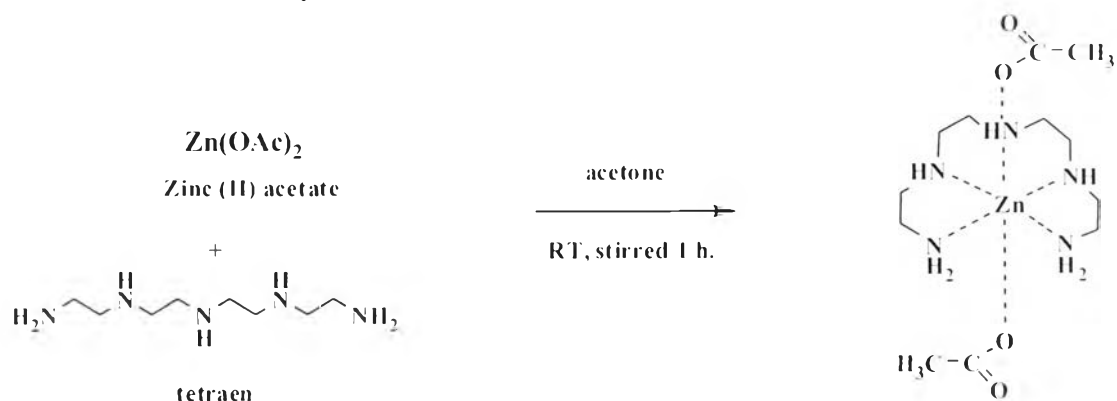
3.2.1.1 Synthesis of Cu(tetraen) Complex



Scheme 3.1 Synthesis of Cu(tetraen) complex

The preparation of metal amine-complexes was done by modification of the method reported in the literature [25, 26]. The mole ratio of copper (II) acetate monohydrate ($\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$): tetraen was 1:1. A solution of tetraen (0.49 ml, 2.59 mmol) was stirred in acetone (20 mL) at room temperature. $\text{Cu(OAc)}_2 \cdot \text{H}_2\text{O}$ (0.51 g, 2.57 mmol) was gradually added to solution and was stirred for 1 hour. The reaction mixture was evaporated to remove acetone and dried under vacuum to obtain Cu(tetraen) as a blue viscous liquid (0.95 g, 95%): FTIR (cm^{-1}): 3252, 3137 (NH stretching), 2946, 2921, 2881 (CH stretching), 1557 (asymmetric C=O), 1392 (symmetric C=O), 1334 (CN stretching), 1007 (CO stretching). Cu(tetraen) shown m/z 370.42, UV; λ_{max} (MeOH) = 264 nm, molar absorptivity (ϵ) = 4,083. Anal. Calc. for $\text{CuC}_{12}\text{O}_4\text{H}_{29}\text{N}_5$: C 38.83; H 7.88; N 18.89; found: C 38.84; H 7.89; N 15.58.

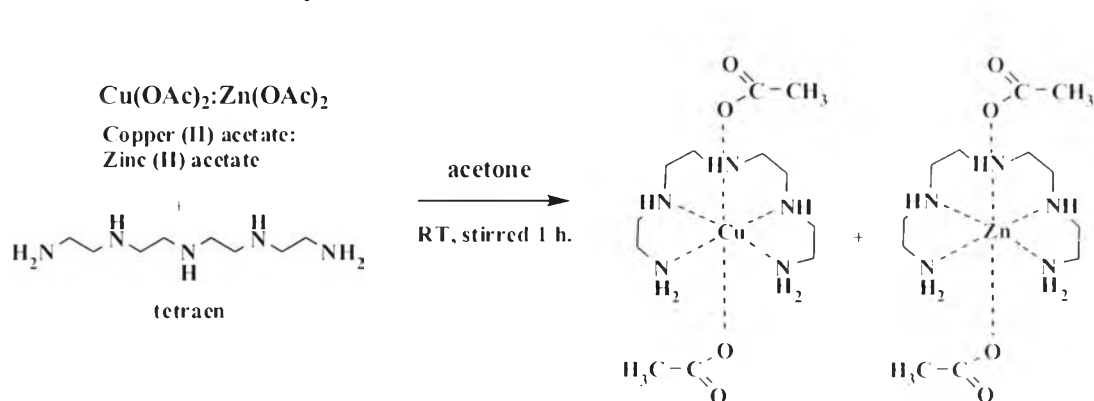
3.2.1.2 Synthesis of Zn(tetraen) Complex



Scheme 3.2 Synthesis of Zn(tetraen) complex

The mole ratio of zinc (II) acetate dihydrate ($\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$):tetraen was 1:1. A solution of tetraen (0.49 mL, 2.47 mmol) was stirred in acetone (20 mL) at room temperature. $\text{Zn(OAc)}_2 \cdot 2\text{H}_2\text{O}$ (0.54, 2.45 mmol) was gradually added to solution and was stirred for 1 hour. The reaction mixture was evaporated to remove acetone and dried under vacuum to obtain Zn(tetraen) as a yellow viscous liquid (0.90 g, 90%); FTIR (cm^{-1}): 3289, 3136 (NH stretching), 2927, 2827 (CH stretching), 1562 (asymmetric C=O), 1388 (symmetric C=O), 1331 (CN stretching), 1003 (CO stretching). Zn(tetraen) shown m/z 390.32, UV; λ_{max} (MeOH) = 203 nm, molar absorptivity (ϵ) = 900. Methanol was used as solvent to measure the absorbance of metal-amine complex due to Zn(tetraen) was difficult to dissolve in water. Anal. Calc. for $\text{ZnC}_{12}\text{O}_4\text{H}_{29}\text{N}_5$: C 38.64; H 7.84; N 18.80; found: C 41.96; H 7.94; N 14.64.

3.2.1.3 Synthesis of Cu(tetraen):Zn(tetraen) Complex



Scheme 3.3 Synthesis of Cu(tetraen):Zn(tetraen) complex

The mole ratio of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}:\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}:\text{tetraen}$ was 0.5:0.5:1. A solution of tetraen (0.48 mL, 2.53 mmol) was stirred in acetone (20 mL) at room temperature. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.25 g, 1.25 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.28 g, 1.45 mmol) was gradually added to solution and was stirred for 1 hour. The reaction mixture was evaporated to remove acetone and dried under vacuum to obtain $\text{Cu}(\text{tetraen}):\text{Zn}(\text{tetraen})$ as a blue viscous liquid (0.93 g, 93%); FTIR (cm^{-1}): 3242, 3150 (NH stretching), 2935, 2924, 2878 (CH stretching), 1557 (asymmetric C=O), 1390 (symmetric C=O), 1332 (CN stretching), 1008 (CO stretching). $\text{Cu}(\text{tetraen})$ and $\text{Zn}(\text{tetraen})$ shown m/z 370.28 and 390.36, respectively, UV: λ_{max} (MeOH) = 263 nm, molar absorptivity (ϵ) = 3,875. Methanol was used as solvent to measure the absorbance of metal-amine complex due to $\text{Cu}(\text{tetraen}):\text{Zn}(\text{tetraen})$ was difficult to dissolve in water. $\text{CuZnC}_{24}\text{O}_8\text{H}_{28}\text{N}_{10}$: C 38.74; H 7.86; N 18.85; found: C 39.66; H 7.93; N 15.60.

3.2.2 Synthesis of Metal-Amine Complexes in Water

3.2.2.1 Synthesis of $\text{Cu}(\text{tetraen})\text{-W}$ Complex

The mole ratio of $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}:\text{tetraen}$ was 1:1. Tetraen (0.49 mL, 2.59 mmol) and polysiloxane surfactant (TEGOSTAB B8460) (0.25 mL) were dissolved in distilled water (2 mL) at room temperature. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.51 g, 2.57 mmol) was gradually added to a solution. The solution was stirred at room temperature for 1 hour. $\text{Cu}(\text{tetraen})\text{-W}$ was obtained as a blue aqueous solution. This solution was further used in the preparation of RPUR foam. Distilled water was used not only as solvent but also as blowing agent in the preparation of polyurethane foam. UV; λ_{max} (MeOH) = 264 nm, molar absorptivity (ϵ) = 1,145.

3.2.2.2 Synthesis of $\text{Zn}(\text{tetraen})\text{-W}$ Complex

The mole ratio of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}:\text{tetraen}$ was 1:1. Tetraen (0.47 mL, 2.47 mmol) and polysiloxane surfactant (0.25 mL) were dissolved in distilled water (2 mL) at room temperature. $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.54 g, 2.45 mmol) was gradually added to a solution. The solution was stirred at room temperature for 1 hour. $\text{Zn}(\text{tetraen})\text{-W}$ was

obtained as a yellow aqueous solution. This solution was further used in the preparation of RPUR foam. UV; λ_{\max} (MeOH) = 203 nm, molar absorptivity (ϵ) = 790.

3.2.2.3 Synthesis of Cu(tetraen):Zn(tetraen)-W Complex

The mole ratio of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}:\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}:\text{tetraen}$ was 0.5:0.5:1. Tetraen (0.48 ml, 2.53 mmol) and polysiloxane surfactant (0.25 mL) were dissolved in distilled water (2.0 mL) at room temperature. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.25 g, 1.25 mmol) and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.28 g, 2.53 mmol) was gradually added to a solution. The solution was stirred at room temperature for 1 hour. Cu(tetraen):Zn(tetraen)-W was obtained as a blue aqueous solution. This solution was further used in the preparation of RPUR foam. UV; λ_{\max} (MeOH) = 263 nm, molar absorptivity (ϵ) = 950.

Other metal-amine complexes and mixed metal-amine complexes were prepared using similar procedure as described above. Composition of starting materials in the preparation of all metal complexes in acetone and water are shown in Table 3.1.

Table 3.1 Composition of starting materials, yield (%) and appearance of metal-amine complexes

Metal complexes	M(OAc) ₂ :tetraen	Wt. of M(OAc) ₂ (g)		Wt. of tetraen (ml)	Yield (%)	Appearance
		M ₁	M ₂			
Cu(tetraen)	1:2	0.35	-	0.61	95	Blue viscous liquid
Zn(tetraen)	1:2	0.37	-	0.64	89	Yellow viscous liquid
Ni(tetraen)	1:2	0.40	-	0.68	79	Purple viscous liquid
Co(tetraen)	1:2	0.40	-	0.60	66	Blown viscous liquid
Mn(tetraen)	1:2	0.39	-	0.61	76	Blown viscous liquid
Cu(tetraen): Zn(tetraen)	1:2	0.17	0.19	0.64	91	Blue viscous liquid
Cu(tetraen): Ni(tetraen)	1:2	0.24	0.31	0.46	83	Blue viscous liquid
Cu(tetraen): Co(tetraen)	1:2	0.17	0.21	0.63	72	Black viscous liquid
Cu(tetraen): Mn(tetraen)	1:2	0.17	0.20	0.63	81	Black viscous liquid
Cu(tetraen)	1:1	0.51	-	0.49	95	Blue viscous liquid
Zn(tetraen)	1:1	0.54	-	0.46	90	Yellow viscous liquid
Cu(tetraen): Zn(tetraen)	1:1	0.25	0.28	0.48	93	Blue viscous liquid
Cu(tetraen)	1:0.5	0.68	-	0.33	53	Blue viscous liquid
Zn(tetraen)	1:0.5	0.70	-	0.30	64	Yellow viscous liquid

3.3 Preparation of Rigid Polyurethane Foam (RPUR Foams)

3.3.1 Preparation of RPUR Foam in Paper Cup Test

All of RPUR foams were prepared with a two-shot methods at room temperature (32 °C). The formulations used are given in Table 3.2. Catalysts, blowing agent, polyether polyol and surfactant were mixed into a 700 ml paper cup. Then, PMDI was added and vigorously stirred at 2000 rpm for 20 s. Cream time, gel time, rise time and tack free time were measured. Cream time or initiation time is the time between the start of mixing and the point at which fine bubbles begin to appear. Gel time is the time of foam begins to gel. Rise time or end of rise time is the time at which the foam stops expanding as observed visually. Tack free time is the time at which the surface can be touched without sticking [28]. RPUR foams were cured in this mold for 48 hours at room temperature before being removed cut and tested.

Table 3.2 RPUR foam formulations at different indexes (in part by weight unit, pbw)

Formulations (pbw*)	NCO Index			
	100	130	150	180
Polyether polyol (Raypol [®] 4221)	100	100	100	100
Catalyst	0.5	0.5	0.5	0.5
Surfactant (TEGOTAB B8460)	2.5	2.5	2.5	2.5
Blowing agent (H ₂ O)	2.0	2.0	2.0	2.0
PMDI (MR-200)	136.4	177.7	204.6	245.6

*pbw: part by weight or 1 gram in 100 grams of polyol

3.3.2 Preparation of RPUR Foam in Aluminum Mold

Catalysts, blowing agent, polyether polyol and surfactant were mixed into a 700 mL paper cup. Then, PMDI was added and vigorously stirred at 2000 rpm for 20 s. The mixture was immediately poured into an open aluminum mold (10 × 10 × 10 cm). After preparation, RPUR foams were kept at room temperature for 48 hours before being removed, cut and tested.

3.4 Metal Complexes Characterization

3.4.1 Infrared Spectroscopy

An Attenuated Total Reflectance Fourier Transform Infrared Spectrometer (ATR-FTIR) Nicolet 6700 was used to compare the functional groups between $M(\text{OAc})_2$ and metal-amine complexes at room temperature. The main peaks of metal-amine complexes appeared at $3137\text{-}3289\text{ cm}^{-1}$ (N-H stretching), $1557\text{-}1562\text{ cm}^{-1}$ (asymmetric C=O stretching) and $1388\text{-}1392\text{ cm}^{-1}$ (symmetric C=O stretching).

3.4.2 Ultraviolet-Visible Spectroscopy (UV-Visible)

UV-Visible spectroscopy was used to measure the absorbance of metal complexes. UV-Vis spectra were recorded on ultraviolet and visible spectrophotometer at room temperature. The samples were scan over range of 200-500 nm. Absorption spectra were obtained on Varian Cary 50 UV-Vis spectrophotometer.

3.4.3 Flame Atomic Absorption Spectrometry

A Varian AA 280FS atomic absorption spectrometer equipped with air/acetylene burner was used for Cu and Zn measurements in metal complexes. The sensitive wavelengths (nm) and lamp currents (mA) for the determination of the samples were as follow: Cu 327.4 and 5.0, and Zn 213.9 and 5.0, respectively. All of the measurements were carried out in using air/acetylene flame at flow rates of 13.50 and 2.00 L/min.

3.4.4 Mass Spectrometry (MS)

Mass spectra were obtained on a micromass Quattro microTM API spectrometer. Electrospray ionization (ESI) was used for identification of metal complexes. MS is a technique that allows the detection of complexes by separating ions by their unique mass (mass-charge ratios) using a mass spectrometer. The method relies on the fact that every compound has a unique fragmentation pattern (mass spectrum). The sample is ionized; the sample ions are separated based on their differing masses and relative abundance.

3.4.5 Elemental Analysis

Elemental analyses were obtained with a Perkin Elmer PE2004 series II. The percentage weight of carbon, hydrogen and nitrogen in metal-amine complexes were determined.

3.5 Rigid Polyurethane Foam (RPUR Foam) Characterization

3.5.1 Infrared Spectroscopy

An ATR-FTIR Nicolet 6700 was used to analyze functional groups on RPUR foams at room temperature. Spectra were recorded between 4000 and 700 cm^{-1} . A background spectrum was first recorded before experiment. The main peaks appeared at 1405-1415 cm^{-1} (isocyanurate carbon-nitrogen stretching), 1725-1735 cm^{-1} (urethane carbonyl stretching) and 2265-2278 cm^{-1} (isocyanate asymmetric stretching) [29-30].

3.5.2 Density

Density of RPUR foams was calculated averaging the mass of foams over volume following the procedure of ASTM D 1621-09. The size of specimen was 3.0 × 3.0 × 3.0 cm dimension.

3.5.3 Universal Testing Machine

Compressive strength of RPUR foams was performed according to ASTM D 1621-09. The instrument used was an Instron/4206. The size of specimen was 3.0 × 3.0 × 3.0 cm dimension. The rate of crosshead movement was fixed at 2.54 mm/min and the preload cell was 0.100 N. The compression stress at 10% strain deformation was calculated.

3.5.4 Thermogravimetric Analysis (TGA)

Thermal stability of RPUR foams was examined by TGA. The measurements were carried out following the ASTM D 3859-09. The apparatus used was

a Perkin-Elmer/TGA 7. RPUR foam samples were heated from room temperature to 600 °C with a heating rate of 10 °C/min under nitrogen atmosphere [31].

3.5.5 Thermal Constant Analysis

Hot Disk Thermal constant Analyzer TPS2500 (Hot Disk AB) was used to determine thermal conductivity of RPUR foams at room temperature. Two specimens were used for determination thermal conductivity value.

3.5.6 Scanning Electron Microscope (SEM)

Morphology of RPUR foam samples were studied on Hitachi/S-4800 scanning electron microscope. The samples were gold-coated before scanning and done at an accelerating of 7.0 kV and magnification levels of 50X and 70X. The samples were observed in parallel and perpendicular to the rise direction [32].

3.5.7 Thermocouple

A thermocouple was used to determine the temperature profile of foaming reaction. The results could be confirmed that the reaction showed exothermic reaction.

3.5.8 Stopwatch

Reaction time; cream time, gel time, rise time and tack free time were investigated by a stopwatch.