



CHAPTER III EXPERIMENTAL

3.1 Materials

All chemicals were reagent grade and used without further purification. 2,4-Dimethylphenol, paraformaldehyde, methylamine, eugenol and cyclohexylamine were purchased from Merck, Germany. Chloroform-*d* was purchased from Aldrich, Germany. Anhydrous sodium sulfate and sodium hydroxide were obtained from Carlo Erba, Italy. Potassium tetrachloroplatinate (II) (K_2PtCl_4), α,α -azobisisobutyronitrile (AIBN), isopropanol, petroleum ether and chloroform were from Wako, Japan. Diethyl ether and 1,4-dioxane were purchased from Labscan, Ireland.

3.2 Measurements

3.2.1 Fourier Transform Infrared (FTIR) Spectrophotometer

Fourier transform infrared (FTIR) spectra were recorded by using a Nicolet Spectrophotometer with 32 scans at a resolution of 2 cm^{-1} . A frequency range of $4000\text{--}400\text{ cm}^{-1}$ was observed by using deuterated triglycerinesulfate detector (DTGS) with specific detectivity of $1 \times 10^9\text{ cm}\cdot\text{Hz}^{1/2}\cdot\text{w}^{-1}$.

3.2.2 Nuclear Magnetic Resonance (NMR)

NMR spectra were obtained from a Varian Mercury 400 MHz spectrometer (USA). The deuterated solvent used was $CDCl_3$. The internal reference for ^1H NMR was tetramethylsilane.

3.2.3 X-ray Diffractometer

Single crystal analysis was collected by a Rigaku RAXIS RAPID diffractometer with a graphite monochromated $Mo\text{-}K_\alpha$ radiation at 296 K. The structure was solved by direct methods (SIR92) and refined by full-matrix least-squares on F^2 with RAPID AUTO program. All non-hydrogen atoms were refined with anisotropic displacement parameters.

3.2.4 UV-Vis Spectrophotometer

UV-Visible spectra were measured by a Shimadzu UV-2550 UV-Vis spectrophotometer. The samples were dissolved in chloroform.

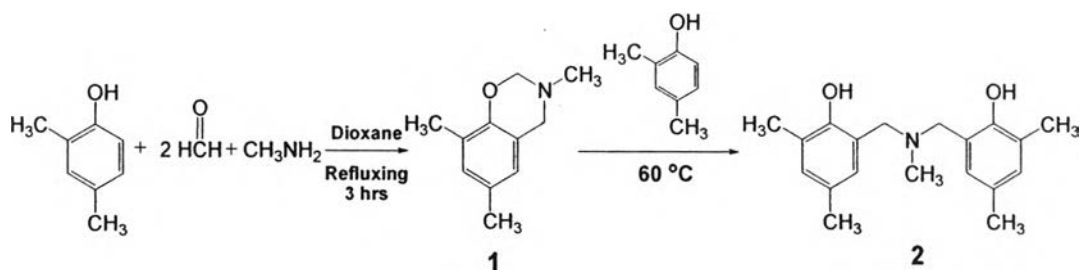
3.2.5 Electrospray Ionization Mass Spectroscopy (ESIMS)

Electrospray ionization mass spectrometry (ESIMS) was recorded by using a MicroTOF LC, Bruker instrument equipped with Bruker Daltonics DataAnalysis 3.3 software with positive mode. Samples were dissolved in chloroform. The capillary voltage was set at 100.0 V.

3.3 Methodology

3.3.1 Complexation of *N,N*-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine and Pt Ions

N,N-bis(2-hydroxy-3,5-dimethylbenzyl)methylamine, **2** was prepared as reported elsewhere (Phongtamrug *et al.*, 2006) and used as a model compound. 3,4-Dihydro-3,6,8-trimethyl-2*H*-1,3-benzoxazine, **1** and 2,4-dimethylphenol (1:1) were mixed and stirred at 60 °C. The mixture was allowed to react until viscous and left for precipitation. The precipitate obtained was collected and washed with diethyl ether before drying. Compound **2** was recrystallized in isopropanol before use. Scheme 3.1 shows the preparation of benzoxazine-based compounds **1** and **2**.



Scheme 3.1

Complexation in Solution

Solutions of **2** in chloroform and potassium tetrachloroplatinate (K_2PtCl_4) in deionized water were prepared. The two solutions were mixed and the mixture was left for a week. The chloroform phase was collected and dried by anhydrous Na_2SO_4 for overnight. The solution was left for crystallization before characterized by UV-Vis spectroscopy, 1H -NMR and Electrospray Ionization Mass Spectroscopy (ESIMS).

Percentage of Metal Ion Extraction

Solutions of K_2PtCl_4 in deionized water (0.5×10^{-4} M) and **2** in chloroform (2.0×10^{-4} , 1.5×10^{-4} , 1.0×10^{-4} , 0.5×10^{-4} , 0.25×10^{-4} , 0.125×10^{-4} , 0.0625×10^{-4} and 0.005×10^{-4} M) were prepared. Each solution was mixed together, vigorously shaken for 1 min, and left for 2 days before analyzing the chloroform phase by UV-Vis spectroscopy. The new peak at 352 nm was measured and calculated for extraction percentage by equation $[(A-A_0)/A] \times 100$ where A is the absorbance after extraction and A_0 is initial absorbance.

Single Crystal of Host-Metal Ion Complex

Solutions of **2** in chloroform and K_2PtCl_4 in deionized water were prepared, vigorously mixed, and left for a week. The organic phase was collected and left until the yellow crystals were obtained. The crystals were used to characterize by single crystal analysis and FTIR.

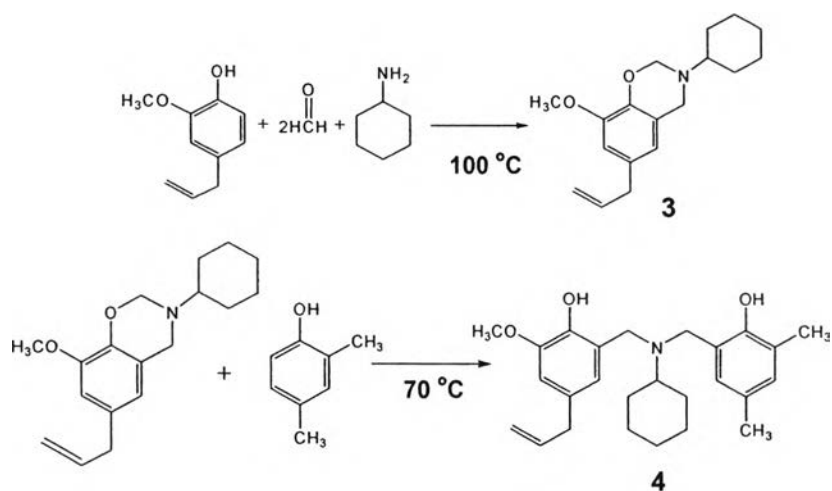
3.3.2 Synthesis of Benzoxazine-based Compounds **3** and **4**

Synthesis of 3,4-Dihydro-6-allyl-3-cyclohexyl-2*H*-1,3-benzoxazine, **3**

Allyl-containing benzoxazine monomer, **3** was prepared by mixing eugenol (12.28 ml, 0.080 mole), paraformaldehyde (4.80 g, 0.160 mole) and cyclohexylamine (9.12 ml, 0.080 mole) heated at 100 °C overnight (Scheme 3.2). Cold methanol was added into the mixture. Then, methanol solution of the mixture was left at 0 °C for precipitation. The precipitates were collected and washed with cold methanol before drying.

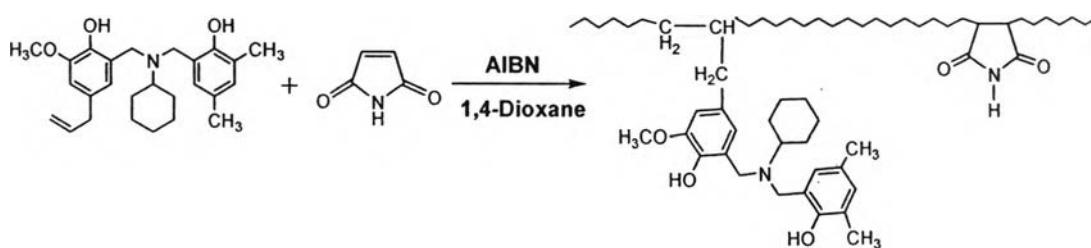
Synthesis of *N*-(2-hydroxy-3-methoxy-5-allylbenzyl)-*N*-(2'-hydroxy-3',5'-dimethylbenzyl)cyclohexylamine, **4**

Allyl-containing benzoxazine dimer, **4** was prepared by mixing **3** (7.46 g, 0.027 mole) and 2,4-dimethylphenol (3.23 ml, 0.027 mole) and heating at 70 °C overnight (Scheme 3.2). The orange viscous obtained was added with petroleum ether and it was left for precipitation. The precipitates were collected and washed with petroleum ether before drying.



Scheme 3.2

3.3.3 Polymerization of **4**



Scheme 3.3

Copolymer **4**-maleimide was prepared by mixing equimolar ratio of **4** (404.46 mg, 0.988 mmol) and maleimide (95.887 mg, 0.988 mmol) in 1,4-dioxane and using AIBN (16.221 mg, 10 mol%) as an initiator (Scheme 3.3). The

polymerization mixture was degassed and heated under nitrogen atmosphere at 55 °C for 2 days. The solvent was removed under reduced pressure. The reaction mixture was precipitated by adding excess amount of diethyl ether. Both precipitate and solution parts were determined the structure by using FTIR.