



Chapter III

Experiment

3.1 Synthesis of the Macrocyclic Polyamide Compounds

3.1.1 Chemicals

1. 1,2-Diaminoethane (Analar grade, Merck)
2. 1,3-Diaminopropane (Analar grade, Merck)
3. Phthalimide (Purum, Fluka)
4. Phosphorus pentachloride (Analar grade, BDH)
5. Palladium on Activated Charcoal (5%Pd, Fluka)
6. Methanol (Analar grade, Merck)
7. Diethyl Ether (Analar grade, Carlo Erba)
8. Carbontetrachloride (Analar grade, Carlo Erba)
9. Absolute Ethanol (Analar grade, Merck)
10. Tetrahydrofuran (Analar grade, Carlo Erba)
11. Nitric Acid (Analar grade, BDH)
12. Sulfuric Acid (Analar grade, BDH)
13. Anhydrous Sodium Sulfate (Analar grade, M&B)
14. Anhydrous Calcium Chloride (Laboratory Grade, Fluka)
15. Potassium Hydroxide (Laboratory Grade, BDH)
16. Lithium Aluminium Hydride (Fluka)

All chemicals except tetrahydrofuran were used without further purification. Tetrahydrofuran was dried initially over solid

potassium hydroxide before being heated under reflux over lithium aluminium hydride and finally fractionally distilled.

3.1.2 Apparatus

John - Fisher electrothermal melting point apparatus with a cover glass sample holder.

UV - Visible spectrophotometer, Shimadzu, Model UV 240 with 10 nm match quartz cells,

Infrared spectrophotometer, Perkin - Elmer, Model Perkin - Elmer 780, with grating infrared spectrophotometer,

Fourier - transform NMR spectrometer, Joel, Model JNX-FX 90 Q,
Mass spectrometer, Joel, Model JMS - DX 300 / JMA 2000, with electron ionization source,

Elemental analyzer, Perkin - Elmer, Model Perkin - Elmer 240 CHNO analyzer,

High performance thin layer chromatography, Camag,

Hydrogenation reactor

3.1.3 Procedure

3.1.3.1 Preparation of 4-Nitrophthaloyl Chloride

4-Nitrophthaloyl chloride could be prepared from phthalimide as starting material. Fuming nitric acid (48 ml, 1.14 mol) was added to concentrate sulfuric acid (280 ml). The mixture was cooled in an ice bath and phthalimide (4 g, 0.27 mol) was stirred in as rapidly as possible while the temperature of the nitrating mixture was kept

between 10°C and 15°C . The clear pale yellow solution was slowly poured with vigorous stirring onto 900 g of cracked ice, the temperature of this mixture must not rise above 20°C . The crude nitrating product was filtered and purified by crystallization from ethanol to yield 4-nitrophthalimide as a yellow solid 53%, mp 198°C .

To a solution of sodium hydroxide (8 g, 0.2 mol) in water (72 ml) was added 4-nitrophthalimide (24 g, 0.125 mol). The mixture was boiled and made barely acid to litmus with concentrated nitric acid. After the neutral point was reached additional nitric acid (21 ml, 0.3 mol) was added. The solution was allowed to cool and extracted with alcohol - free ether. After the extracted solvent was dried over anhydrous sodium sulfate the ether was removed to give practically white crystals of 4-nitrophthalic acid melting at $163 - 164^{\circ}\text{C}$, the yield was 98%.

4-Nitrophthalic acid (19 g, 0.1 mol) was mixed with phosphorus pentachloride (38 g, 0.18 mol) in 100-ml round bottom flask equipped with a calcium chloride guard-tube which was connected to a gas absorption device. The flask was heated at 130°C , with occasional shaking until the reaction commenced and then for 30 minutes further. A pale yellow homogeneous solution was formed. Phosphorus oxychloride (bp 107°C) was removed by gradually heating in an oil bath to $200 - 220^{\circ}\text{C}$ and allowed to solidify. 4-nitrophthaloyl chloride was obtained as a white crystalline solid (55%), mp 112°C .

3.1.3.2 Preparation of 3,4-(4'-nitrobenzo)-1,6-diazacycloocta-3-en-2,5-dione (Ia)

A 1 - litre, three - necked round bottom flask equipped with condenser, nitrogen blanket and two dropping funnels was previously placed with dry tetrahydrofuran (400 ml) and stirred vigorously. Two solutions of 4-nitrophthaloyl chloride (2.5 g, 0.01 mol) in 200 ml of dry tetrahydrofuran and 1,2-diaminoethane (1.4 ml, 0.02 mol) in 200 ml of dry tetrahydrofuran were added simultaneously over 3-4 hours period at room temperature. After the addition was complete, the resulting suspension was stirred slowly overnight. The white solid was filtered, recrystallized from water - methanol and dried under vacuum to give a white solid of 3,4-(4'-nitrobenzo)-1,6-diazacycloocta-3-en-2,5-dione (48%), dec 102°C.

3.1.3.3 Preparation of 3,4-(4'-aminobenzo)-1,6-diazacycloocta-3-en-2,5-dione (Ib)

In water solution (150 ml) of 3,4-(4'-nitrobenzo)-1,6-diazacycloocta-3-en-2,5-dione (4.0 g, 0.16 mol), palladium carbon (1.6 g, ca.0.0128 mol) was suspended and then the mixture was stirred at room temperature under a hydrogen pressure of 5 atm in the reactor. After the hydrogen absorption ceased the palladium carbon was filtered off. The filtrate was evaporated giving a slightly yellowish solid which was recrystallized from hot methanol to yield the desired product (40%), dec 85°C

3.1.3.4 Preparation of 3,4-(4'-nitrobenzo)-1,6-diazacyclonona-3-en-2,5-dione (IIa)

The synthetic procedure of this compounds using 4-nitrophthaloyl chloride was similar to that of 3,4-(4'-nitrobenzo)-1,6-diazacycloocta-3-en-2,5-dione as described in 3.1.3.2 but using 1,3-diaminopropane instead of 1,2-diaminoethane. The product was a white solid (45%), dec 110°C.

3.1.3.5 Preparation of 3,4-(4'-aminobenzo)-1,6-diazacyclonona-3-en-2,5-dione

The procedure was similar to the synthesis of 3,4-(4'-aminobenzo)-1,6-diazacycloocta-3-en-2,5-dione (3.1.3.3). 3,4-(4'-nitrobenzo)-1,6-diazacyclonona-3-en-2,5-dione was reduced in the reactor to yield the product as white solid (35%), dec 95°C

Several attempts to reduce polyamide to polyamine compounds were tried but in all cases the product indicated the ring fission.

3.2 Complex Formation Study of the Synthetic Macrocyclic Polyamide Compounds

3.2.1 Chemicals

Doubly distilled water was used throughout this experiment. A 2×10^{-3} M solution of synthetic macrocyclic polyamides were prepared by dissolving the corresponding compounds in water. The metal

nitrate (reagent grade) were used to prepare 2×10^{-4} M solutions of metal ions. Chloroform was shaken three times with 2 M hydrochloric acid, 2 M sodium hydroxide and distilled water, dried with anhydrous sodium sulfate and distilled. Other reagents were of reagent grade.

3.2.2 Apparatus

Extraction was done by using Mechanical Shaker, Model HS 500 (Jankel & Kunkel). Shimadzu Double - Beam Digital Atomic Absorption/Flame Emission Spectrophotometer, Model AA 650 was used for the determination of most metal ion concentrations. The pH of aqueous phase was measured with a Radiometer Copenhagen PHM 83 Autocal pH meter. Complex formation was investigated conductometrically and the conductivity was measured using CG 854 type Schott Geräte Conductometer.

3.2.3 Extraction of Various Metals with the Synthetic Macro-cyclic Polyamide Compounds

Equal volumes (10 ml) of chloroform and mixed aqueous solutions of 2×10^{-3} M synthetic macrocyclic polyamide compound, and 2×10^{-4} M metal nitrate were placed in an 8-dram vial. The vial was shaken for 1 hour at 200 strokes/min at room temperature. After the phase separation had occurred and the concentration of the metal ion in aqueous phase was measured by atomic absorption spectrophotometer at the resonance line for each metal.

3.2.4 Complex Formation of Synthetic Macrocyclic Polyamide
- Pb(II) Complexes

The conductivity of the lead nitrate - macrocyclic polyamide aqueous solution was measured at room temperature. The concentrations were 1×10^{-4} M for lead nitrate and $(0-3) \times 10^{-4}$ M for synthetic macrocyclic polyamide compounds, the molar ratio of synthetic macrocycle to metal being changed from 0 to 3.