CHAPTER II

EXPERIMENTAL

2.1 Synthesis of Macrocyclic and Open-chain Schiff-base Compounds

Chemicals

1. Salicylaldehyde   (Purum , Fluka)

2. Sodium hydroxide   (Laboratory grade , Eka)

3. 1,2-Diaminoethane   (Analar grade , Carlo Erba)

4. 1,3-Diaminopropane   (Analar grade , Merck)

5. 1,2-Dibromoethane   (Analar grade , Aldrich)

6. 1,3-Dibromopropane   (Analar grade , Merck)

7. Ethanol   (Analar grade , Merck)

8. Absolute methanol   (Analar grade , J.T. Baker)

9. Diethyl ether   (Analar grade , J.T. Baker)

10. Chloroform   (Analar grade , Merck)

11. Petroleum Spirit 40-60 ^{o}c (Analar grade , BDH)

Instruments and Apparatus

1. John-Fisher electrothermal melting point apparatus
2. Infrared spectrophotometer,Perkin-Elmer,Model 781
3. Fourier transform NMR spectrometer,Jeol,Model TNX-FX 90 Q
4. Mass spectrometer,Jeol,Model JMS-DX 300/JMA 2000
5. Elemental analyzer, Perkin-Elmer , Model 240 CHNO analyzer

Procedure

2.1.1 Preparation of Bis(salicylaldehyde)N,N-ethyl-enediimine ; Salen

To a stirred solution of 1,2-diaminoethane (3.74 mL, 0.05 mole)in ethanol (45 mL) was added dropwise of salicyl-aldehyde (12.05 mL,0.11 mole) at 0 ^{o}c.   If the mixture was so hard , adding a few mL of ethanol was necessary. Then the mixture was stirred further for 5 minutes.   The yellow precipitate was filtered and recrystallized from warm ace-tone to obtain the pure product.   The yield is 12.3 g. (91.79 %); mp 120-121 ^{o}c.   Anal.Calcd for $C_{16}H_{16}N_2O_2$: C,71.64 ;H,5.97;N,10.45. Found :C,71.61 ;H,6.05 ;N,10.41.

2.1.2 Preparation of Bis(salicylaldehyde)N,N-tri-
methylenediimine ; Saltn

The procedure was similar to that described above
(2.1.1),using1,3-diaminopropane(4.42mL,0.05mole) , instead
of 1,2-diaminoethame,in methanol (50 mL) and salicylal-
dehyde (12.05 mL,0.11 mole).   Cooling was not nescessary.
The yellow precipitate was produced,filtered and recrys-
talized from petroleum spirit 40-60 ^{o}c. The yield is
12.4 g.(87.94 %); mp. 50-51°c. Anal.Calcd for $C_{17}H_{18}N_2O_2$
: C,72.34 ;H,6.38 ;N,9.93. Found :C,72.19 ;H,6.35 ;N,9.73.

2.1.3 Praparation of 3,4,9,10-Dibenzo-1,12-diaza-5,
8-dioxacyclopentadecane-1,11-diene ; O-en-N-tn

2.1.3.1 Preparation of 1,4-Bis(2-formylphenyl)-1,
4-dioxabutane ; O-en

In one litre round bottom flask was placed a
solution of salicylaldehyde (31.4 mL,0.3 mole) in ethanol
(30 mL).   Nitrogen gas was purged into the solution for 5
minutes,then sodium hydroxide (12.0 g.,0.3 mole) in dis-
tilled water approximately 300 mL was added to the stirred
solution above 67 ^{o}c until the mixture was completely
dissolved and 1,2-dibromoethane (14.30 mL,0.15 mole) was
added. The sufficient ethanol was added to produce a homo-
geneous solution. The solution was refluxed under nitrogen

for 50 hrs, then cooled and let stand at 0 $^{\circ}$c. The cream-colored product was filtered, washed with water and recrytallized from ether-chloroform mixture(50:50) ; yield 18.15 g. (44.8 %); mp 123-124 $^{\circ}$c. Anal.Calcd for $C_{16}H_{14}O_4$: C,71.11 ;H,5.19. Found : C,71.04; H,5.23.

2.1.3.2 Preparation of O-en-N-tn

In a solution of O-en (2.7 g,0.01 mole)in absolute methanol (150 mL) was added dropwise of 1,2-diaminopropane (0.67 mL,0.01 mole) in absolute methanol (30 mL). The solution was refluxed for 50 mins, cooled down to room temperature. Then the solution was added cold water (300 mL) and the colloid was let stand at 0 $^{\circ}$c. The obtained white product was filtered,washed with water and recrystallized from ether. The yield is 2.86 g.(92.86 %); mp 149-150 $^{\circ}$c. Anal.Calcd for $C_{19}H_{20}N_2O_2$: C,74.03 ;H,6.49 ; N,9.09. Found : C,74.19 ;H,6.62 ;N,9.08.

2.1.4 Preparation of 3,4,10,11-Dibenzo-1,13-diaza-5,9-dioxacyclohexadecane-1,12-diene ; O-tn-N-tn

2.1.4.1 Preparation of 1,5-Bis(2-formylphenyl)-1, 5-dioxapentane ; O-tn

The procedure was similar to the synthesis of O-en (2.1.3.1) , using 1,3-dibromopropane (15.3 mL,0.15 mole)

instead of 1,2-dibromoethane. The reaction time was 45 hrs. The analogous product was as white needles. The yield is 25.47 g. (59.8 %); mp 91-92 $^{\circ}$c. Anal.Calcd for $C_{17}H_{16}O_4$: C,71.83 ;H,5.63. Found :C,71.73 ;H,5.75.

2.1.4.2 Preparation of O-tn-N-tn

The procedure was similar to the synthesis of O-en -N-tn (2.1.3.2) , using O-tn (2.84 g.,0.01 mole) in abso- lute methanol (150 mL) in stead of O-en and 1,3-diamino- propane (0.83 mL,0.01 mole) in absolute methanol (30 mL). The reaction time was 3 hrs. The mixture was let stand at 0 $^{\circ}$c and then excess cold water was added until the white precipitate was produced. The product was recrys- talized from petroleum spirit 40-60 $^{\circ}$c. The yield is 0.95 g. (29.5 %) ; mp 155-157 $^{\circ}$c. Anal.Calcd for $C_{20}H_{22}N_2O_2$: C,74.53 ;H,6.88 ;N,8.70. Found: C,74.53 ;H,6.88 ;N,8.85.

2.2 Complex Formation Study of the Synthetic Schiff-base Compounds

Chemicals

Doubly distilled water was used throughout this experiment. A 5 x 10^{-4} M solution of the synthetic Schiff -base compounds was prepared in chloroform. The metal nitrates of analar grade were used to prepare 1 x 10^{-4} M

aqueous solution of metal ions .

Instruments and Apparatus

1. Atomic Absorption/Flame Emission Spectrophotome-
    ter, Shimudzu, Model AA 670 was used for the de-
    termination of metal ion concentration.

2. Digital Ionalyzer,Orion Research,model 701A pH
    meter was used for adjustment the pH of aqueous
    solution.

3. UV/Visible spectrophotometer,Jasco,Model UVIDEC-
    650 was used for stoichiometric study of complex
    in solution.

4. Horizontal shaker , IKA-WERK , Model HS-500.

2.2.1 Solvent Extraction

10 mL aliquot of aqueous phase containing 1×10^{-4} M
metal ion was shaken with an aqual volume of chloroform
phase containing 5×10^{-4} M Schiff-base compound in an 8-dams
vial for 1 hr. at 220 strokes/min at room temperature.
Prior to extraction, the pH of each solution in aqueous
phase was adjusted to the desired value by using appro-
priate solution as listed in Table 2.1.   After phase se-
paration, the concentration of metal ion in the aqueous
phase was determined by atomic absorption spectrophoto-
meter and corresponding extraction percentage was calcu-

lated. Obtained values were tabulated in Table 3.7.

Table 2.1   pH values and compositions of reagent
solutions at room temperature

pH	Solutions
2.2	5×10^{-3} M HCl + 9×10^{-3} M KCl, diluted to 1 litre
3.4	5×10^{-3} M glacial acetic acid and 5×10^{-3} M.sodium acetate in ratio 950 to 50 mL
4.5	5×10^{-3} M glacial acetic acid and 5×10^{-3} M sodium acetate
5.9	5×10^{-3} M glacial acetic acid and 5×10^{-3} M sodium acetate in ratio 50 to 950 mL
7.2	0.05 % w/v Sodium acetate
8.1	1×10^{-3} M ammonium hydrogen phosphate
9.7	5×10^{-3} M ammonia solution and 5×10^{-3} M ammonium chloride made up to 1 litre with deionized water.

2.2.2   Optimum Wavelength of Complex in Absolute
Methanol

Optimum wavelength of complex: Cu(II)-Salen,Cu(II)-
Saltn,Cu(II)-[O-en-N-tn],Cu(II)-[O-tn-N-tn] were determined
in absolute methanol by keeping Schiff-base compound at con-
centration of 5×10^{-4}M and varying Cu(II) concentration from
0 to 7×10^{-4} M.   The spectral changes of each concentration
were carried out by UV-Visible spectrophotometric method.

2.2.3 Stoichiometric and the Apparent Stability
Constant Study of Complex in Absolute Methanol

Copper nitrate was selected for stoichiometric stu-
dy with all of the synthetic Schiff-base compounds.   A se-
ries of Cu(II) and Schiff-base compound mixtures in abso-
lute methanol containing various mole fractions of Cu(II)
from 0-1 were prepared. The sum of the concentration of
Cu(II) and that of Schiff-base compound was kept constant
at 1×10^{-3} M .   The absorbances of Cu(II)-Salen mixture ,
Cu(II)-Saltn mixture,Cu(II)-[O-en-N-tn] mixture and Cu(II)
-[O-tn-N-tn] mixture were measured against chloroform   at
562 nm,356 nm,352 nm and 364 nm,respectively. The apparent
stability constant was calculated from the results above
and reported in Table 3.8.

2.3   Possibility of Copper Determination Using   Bis
      (Salicylaldehyde)N,N'ethylenediimine   as   Spec-
      trometric Reagents   by   Chloroform   Extraction

Instruments

The absorption was measured,as described in section 2.2, by UV/Visible spectrophotometer.   The pH meter and horizontal shaker were also used in this experiment.

Reagents

1. Stock solution of 2.5×10^{-2} M Salen in chloroform
2. Stock standard solution of 1×10^{-3} M Copper as copper nitrate , pH adjusted to 7.2
3. Copper standard solution 1000 + 0.002 g/l (Merck)

2.3.1 Optimum Condition Study

Procedure

The optimum conditions for Cu determination using Salen as complexing reagent by chloroform extraction were studied in order of selected wavelength, optimum reagent concentration,shaking time,shaking stroke and standing time.

Selected Wavelength

Equal volume(10 mL) of Salen in chloroform phase was fixed at 5×10^{-3} M while Cu concentration in aqueous phase at pH 7.2 was varied from $(1.0-7.0) \times 10^{-3}$ M . After shaking for 1 hr at 220 strokes/min and waiting until the phase separation was completed, the chloroform layer was transfered for spectral study in the range 300 to 800 nm using chloroform as reference.

Effect of Reagent Concentration

A series of solutions containing 1.0×10^{-3} M of Cu in aqueous phase and various Salen concentrations in chloroform phase varying from 4.0×10^{-4} to 2.0×10^{-2} M, was studied by using 1 hr shaking time , 220 shaking stroke. The absorbances of the chloroform layer were plotted at 562 nm.

Effect of Shaking Time

The procedure for chloroform extraction was similar to that of previously described,using 1.0×10^{-3} M of Cu solution,1.0×10^{-2} M of Salen, 220 strokes/min and shaking times were varied from 5 - 60 mins.

Effect of Shaking Stroke

The procedure for chloroform extraction was similar to that of previously described, using 55 mins shaking time and shaking stroke was varied from 100-260 strokes/min.

Effect of Standing Time

The absorbances of the Cu(II)-Salen complex solutions in chloroform layer were measured periodically at a specific time interval after shaking. The mixtures were allowed to stand for phase separation and 5 mL of each of chloroform phase were then taken from the vial for measurement. The standing time was varied from 2 mins to 6 hrs.

2.3.2 Study of the Working Range for Determination by Using Salen as Spectrometric Reagent

The absorbances of chloroform layer were subsequently measured at 562 nm, using optimum conditions that obtained in section 2.3.1. Salen concentration in chloroform phase was kept constant at 1×10^{-2} M. A range of 0-88 ppm Cu(II) was prepared in aqueous solution at pH 7.2.

2.3.3   Conformation of Beer-Lambert's Law and Accuracy Measurement of Copper Using Salen as Spectrometric Reagent

Using a procedure similar to that described in section 2.3.2 and also using the optimum conditions that obtained in 2.3.1, Salen concentration in chloroform layer was kept constant at 1×10^{-2} M . A range of 1-15 ppm Cu(II) was selected for calibration curve. Copper solution of known value (12 ppm) was used for accuracy and precision measurement in term of % error and % Relative Standard Deviation (RSD), respectively.

2.3.4   Effect of Interfering Ions

Cadmium and manganese in the term of nitrate salt were selected as possible interfering metal ions. The effect of coexisting ions was measured at 10.00 ppm Cu(II). Mole ratio of Cu(II) to coexisting ion was 50:1 to 1:50. The absorbances of the solution in chloroform layer were measured at 562.0 nm and compared with the absorbances of Cu(II) alone (10.00 ppm).

2.3.5   Application of The Method to The Determination of Copper in Solder Ingot

The presently developed method was applied to the determination of Cu(II) in solder ingot

Procedure

Exactly 0.2-0.3 g of finely divided sample was weighed and transfered to a 150 mL beaker. Rapidly add warm reagent solution* (15 mL)into the beaker, cover with a watch glass. The sample solution was warmed until it was clear,cooled to the room temperature. It was quantitatively transfered into a 100 mL volumetric flask and made up to the mark with distilled water. The freshly prepared solution (20 mL) was pipetted into 50 mL beaker and the pH of solution was adjusted to 4.5 with 50 % NaOH solution. This sample solution was transfered into a 50 mL volumetric flask and diluted with distilled water.

* Reagent solution : 45 mL of conc.fluoroboric acid, 95 mL of conc.nitric acid and 45 mL of 1% w/v tartaric acid solution were mixed simultaneously in a 200 mL beaker, then it was made up to 200 mL with distilled water in volumetric flask.

Calibration of Standards

Calibration curve of standards were prepared in the range of 1-10 ppm Cu in 25 mL volumetric flask. Each of standard solution was adjusted to pH 4.5.

Chloroform Extraction

Equal volume (10.00 mL) of Salen in chloroform phase, 1.0×10^{-2} M, and copper solution in the range of 1-10 ppm were pipetted into each vial. Chloroform extraction of sample solution was similar to those of standard copper solutions, using optimum conditions obtained in 2.3.1 . The absorptions in chloroform layer were measured at 562 nm. Percentage of copper in solder ingot was determined from the calibration curve.